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(71) Applicant: **Facultes Universitaires Notre-Dame de
la Paix
5000 Namur (BE)**

(72) Inventors:
• **Nagy, Janos B., Pr.
5100 Jambes (BE)**
• **Nagaraju, Narasimaiah, Dr.
Jayanagar, 560083 Bangalore (IN)**
• **Willems, Isabelle
5150 Soye (BE)**
• **Fonseca, Antonio, Dr.
1348 Louvain-La Neuve (BE)**

(74) Representative: **Van Malderen, Joelle et al
Office Van Malderen,
Place Reine Fabiola 6/1
1083 Bruxelles (BE)**

(54) **Catalyst supports and carbon nanotubes produced thereon**

(57)   The present invention is related to single and/or multiple-wall carbon nanotubes which may contain interstitial metals obtainable by a preparation process, comprising a catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said support comprising hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

The present invention is also related to carbon fibres obtainable by said preparation process.

The present invention also pertains in particular to said catalytic system and to said preparation process.

Another aspect concerns the use of the nanotubes and of the catalytic system according to the invention.
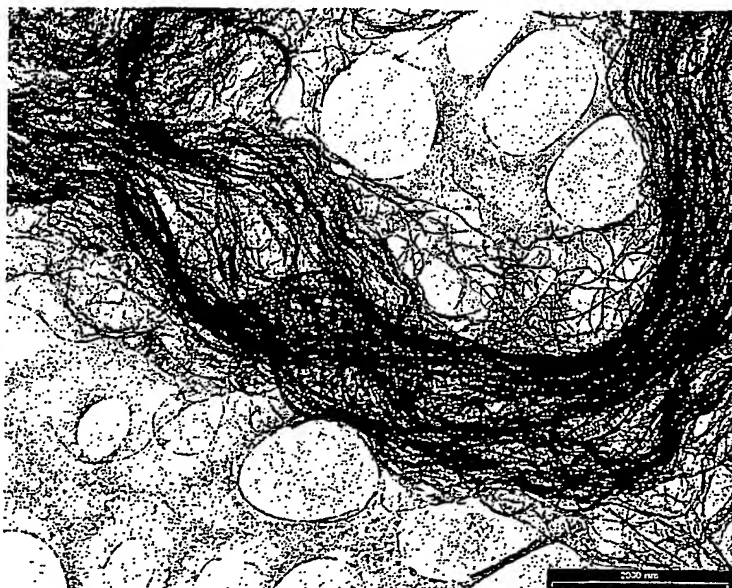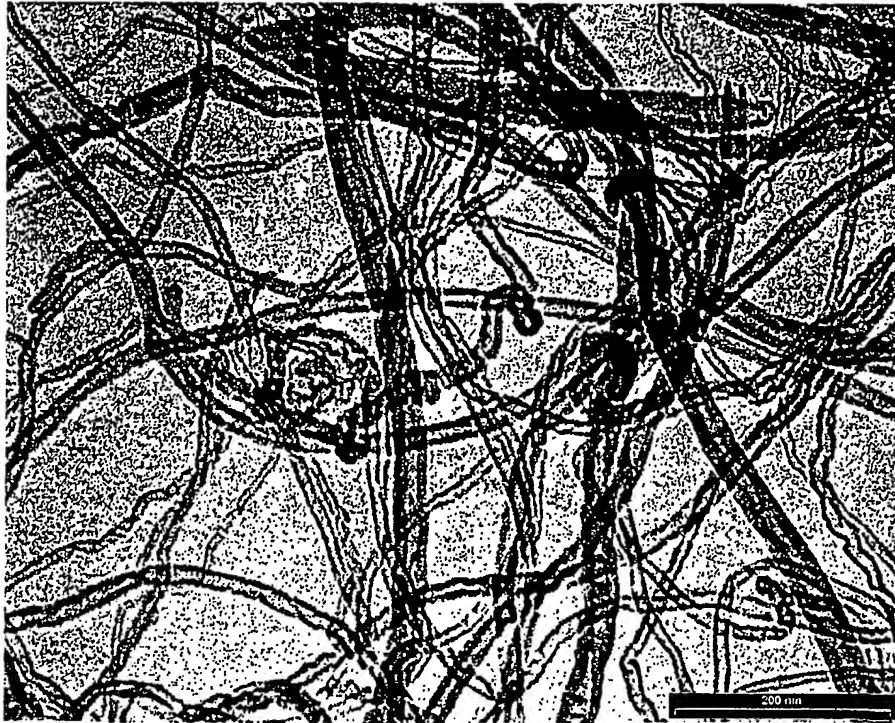
Fig.3a

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Fig.3b

Description

Field of the Invention

[0001]   The present invention is related to the field of single and multiple-wall carbon nanotubes.

[0002]   More precisely, the present invention is related to hydroxide and carbonate-based supported catalysts for carbon nanotube preparation.

State of the art

[0003]   Carbon nanotubes were first observed by Iijima in 1991 (S. Iijima, *Nature* **354**, 56-58 (1991)).

[0004]   Carbon nanotubes can be produced for example, by arc discharge, by laser ablation or by catalytic decomposition of hydrocarbons.

[0005]   The production of carbon nanotubes by the arc discharge and the laser ablation techniques can be carried out either in the absence of catalysts to produce multi-wall nanotubes (MWNTs) or in the presence of catalysts to produce both MWNTs and single-wall nanotubes (SWNTs), together with soot, amorphous carbon and encapsulated metal nanoparticles. The catalyst comprises generally metals, metal oxides or other metal derivatives or mixtures thereof. Examples of those metals are ie., Co, Fe, Ni, V, Mo, Sn, ...

[0006]   The invention discloses the preparation of carbon nanotubes by the catalytic decomposition of hydrocarbons, a technique called CCVD (Catalytic Carbon Vapour Deposition), carried out in the presence of catalysts to produce both MWNTs and SWNTs. Soot and encapsulated metal nanoparticles are the other by-products. The hydrocarbon can be acetylene, ethylene, butane, propane, ethane, methane or any other gaseous or volatile carbon containing compound. The catalyst, for example transition metal, is generally, either pure or dispersed on a support.

[0007]   The presence of a support for the catalyst affects the activity of the catalysts tremendously in the formation of carbon nanotubes. The selectivity of the catalyst for the production of nanotubes also depends on the type of catalyst support interaction.

[0008]   The most common supports used to prepare supported catalyst for carbon nanotubes production are oxides [i.e., silica (P. Piedigrosso *et al., Phys. Chem. Chem. Phys.* **2**, 163-170 (2000)), alumina (I. Willems *et al., Chem. Phys. Lett.* **317**, 71-76 (2000)), silica-alumina mixtures (Kukovecz, A. et al., *Phys. Chem. Chem. Phys.* **2**, 3071-3076 (2000)), magnesium oxide (J.-F. Colomer et *al., Chem. Phys. Lett.* **317**, 83-89 (2000)), calcium oxide (C. Ping et al., CN 1170631 A 19980121), titanium oxide (V. Curtis, et al., Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000), cerium oxide (L. Ji et al., Appl. Chem. **72**, 327-331 (2000)), zeolites (K. Hernadi et al., *Zeolites* **17**, 416-423 (1996)), clays (A. Fonseca et al., *Appl. Phys. A* **67**, 11-22 (1998)), spinels (A. Govindaraj et al., *J. Mater. Res.* **14**, 2567-2576 (1999)), ALPOs (Wang, N. et al., Nature **408**, 50-51 (2000))] and graphite (V. Ivanov et al., *Carbon* **33**, 1727-1738 (1995)).

[0009]   The use of porous materials (i.e., silica, alumina, zeolites, etc.) as supports for catalysts, contaminates the carbon nanotubes produced thereon with a large amount of soot and amorphous carbon, while dissolving the support during the purification of the carbon nanotubes.

[0010]   The catalyst supports used in the present invention do not present the drawbacks of the catalyst supports of the state of the art.

Preliminary definitions

[0011]   The term "metal" stands for a single metal (i.e., Co, Fe, Ni, Cu, V, Mo, ...) or a mixture of two or more metals.

[0012]   The "catalyst" comprises generally metal, metal oxides or other metal derivatives or mixtures thereof.

[0013]   It is meant by "supported catalyst" a material which is produced by mixing the catalyst with the support. During the initial heating, water and other volatile compounds are eliminated from the supported catalyst while the active catalyst is being formed.

[0014]   The wordings "active catalyst" refers to any metal, metal oxide or other metal-derivatives formed during the initial heating of the supported catalyst by the reaction between the support, the catalyst and the gases. The active catalyst is responsible for the carbon nanotube production by CCVD

[0015]   The aluminium alkoxide or any other aluminium salt is also called hereafter "aluminium hydroxide precursor".

[0016]   "CCVD" is the English abbreviation for Catalytic Carbon Vapour Deposition and refers to a catalytic decomposition of hydrocarbons.

[0017]   The "hydrocarbon" can be acetylene, ethylene, butane, propane, ethane, methane or any other gaseous or volatile carbon containing compound.

[0018]   The expression "Crude nanotubes" refers to a mixture of carbon nanotubes and spent supported catalyst.

[0019]   The "carbon material" is made of SWNTs, MWNTs, carbon fibers, carbon nanoparticles, amorphous carbon,

pyrolytic carbon and soot in variable weight ratios.

Aims of the Invention

[0020] The present invention aims to provide hydroxides and carbonates as efficient catalyst supports for catalysts to produce carbon nanotubes by CCVD.

[0021] Furthermore, the present invention presents a method to eliminate the spent supported catalyst from the carbon nanotubes produced without introducing amorphous carbon while dissolving the catalyst support.

[0022] An additional aim of the present invention is to provide a method for producing Al, Mg, Ca, Ce, La and Ti containing carbon nanotubes and to disclose an easy and rapid method for purification of the carbon nanotubes produced on supported catalysts based on the above mentioned supports.

Summary of the Invention

[0023] The present invention is related to single and/or multiple-wall carbon nanotubes which may contain interstitial metals obtainable by a preparation process, comprising at least catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said support comprising hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

[0024] Preferably, the interstitial metals present in the multi-wall nanotubes are selected from the group consisting of Al, Mg, Ca, Ce, La, and Ti.

[0025] A further key aspect of the present invention are carbon fibres obtainable by a preparation process, comprising at least a catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said support comprising hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

[0026] Another key aspect of the present invention is related to carbon nanotubes and/or carbon fibres characterised in that the support of the catalytic system comprises carbonates selected from the group of $CaCO_3$, $MgCO_3$, $Al_2(CO_3)_3$, $Ce_2(CO_3)_3$, $Ti(CO_3)_2$, $La_2(CO_3)_3$ and/or mixtures thereof as well as hydroxides selected from the group of $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Ce(OH)_4$, $Ti(OH)_4$,$La(OH)_3$ and/or mixtures thereof and oxides selected from the group consisting of Al_2O_3, CaO, MgO, CeO_2, TiO_2, SiO_2 and/or mixtures thereof.

[0027] A part of the present invention is a catalytic system for the preparation of single and/or multiple-wall carbon nanotubes and/or for the preparation of carbon fibres, said catalytic system comprising a dispersion of nanoparticles containing metals at any oxidation state in hydroxides and/or carbonates or mixtures thereof and said metals being selected from the group consisting of Fe, Co, Ni, V, Cu, Mo, Sn and/or mixtures thereof.

[0028] In a first embodiment of the present invention, a process is disclosed for the preparation of single and/or multiple-wall carbon nanotubes and carbon fibers comprising at least a catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said catalyst being selected from the group consisting of metals and/or metal oxides and/or metal derivatives characterised in that said support is selected from the group consisting of hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

[0029] In a preferred embodiment of the present invention, said carbonates are selected from the group consisting of $CaCO_3$, $MgCO_3$, $Al_2(CO_3)_3$, $Ce_2(CO_3)_3$, $Ti(CO_3)_2$, $La_2(CO_3)_3$ and/or mixtures thereof and the hydroxides are selected from the group consisting of $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Ce(OH)_4$, $Ti(OH)_4$,$La(OH)_3$ and/or mixtures thereof, said oxides being selected from the group consisting of Al_2O_3, CaO, MgO, CeO_2, TiO_2, SiO_2 and/or mixtures thereof.

[0030] In a second embodiment of the present invention, the preparation process is characterised in that the catalytic step is performed between 500 and 900°C in order to prepare multi-wall nanotubes and between 900 and 1100°C in order to prepare single-wall nanotubes.

Short description of the drawings

[0031] Fig.1 represents the weight loss of the supported catalyst SCA2 (see Table 1) as a function of the heating time under N_2 flow at 700, at 800, at 900 and at 1000 °C. 250 mg of SCA2 were used in each experiment under a nitrogen flow of 300 ml/min. The dotted lines a-g represent the theoretical successive weight losses.

[0032] Fig.2 represents results from acetylene decomposition at 700 °C on SCA2, both in continuous and in discontinuous processes.

[0033] Fig.3a represents a low magnification Transmission Electron Microscopy (TEM) image of as made MWNTs, synthesised by acetylene decomposition at 700 °C in a continuous reaction of 60 min, on the supported catalyst SCA2. The catalyst was activated by preheating 10 min in N_2 flow.

[0034] Fig.3b represents a higher magnification TEM image of MWNTs synthesised as in Figure 3a.

[0035] Fig.3c represents a low magnification TEM image of as made carbon fibers, synthesised by acetylene decomposition at 700 °C in a continuous reaction of 60 min, on the supported catalyst SCA63 (see Table 6a). The catalyst

was activated by preheating 10 min in N_2 flow.

[0036] Fig.3d represents a low magnification TEM image of purified SWNTs, in bundles, synthesised by CH_4/H_2 decomposition at 1000 °C for 6 min, on the supported catalyst SCC81 (see Table 8b). The catalyst was activated by 4 min of in situ preheating from 25 to 1000 °C in a CH_4/H_2 flow.

[0037] Fig.4a represents the inner and outer diameter distribution histograms of the MWNTs synthesised as in Figure 3a.

[0038] Fig.4b represents the number of walls as a function of the inner diameter distribution of the MWNTs synthesised as in Figure 3a.

[0039] Fig.5 contains results from ethylene decomposition on SCA2 (activated by preheating 10 min in N_2 flow) in a discontinuous process at 700, at 800 and at 900 °C. A result of ethylene decomposition at 700 °C in a continuous process is also represented.

[0040] Fig.6 contains results from ethane decomposition on SCA2 (activated by preheating 10 min in N_2 flow) in a continuous process at 700, at 800 and at 900 °C. Results of ethane decomposition at 800 °C in a discontinuous process are also represented.

[0041] Fig.7 contains results from methane decomposition on SCA2 (activated by preheating 10 min in N_2 flow) in a discontinuous process at 900 and at 1000 °C.

[0042] Fig.8 contains results of methane decomposition for 6 min on SCA2 (activated by 4 min of in situ preheating from 25 to 900-1000 °C in a CH_4/H_2 flow) in the presence of hydrogen at 900-1100 °C.

Detailed description of the invention

[0043] The aluminium hydroxide ($Al(OH)_3$) used in the present invention to prepare the catalyst support is preferably a commercial powder (Acros Organics) of variable particle size. The particle size can be very small (ca. 1nm) or very large (ca. 1 mm). In the case of large particles the size distribution is always broader. It can also be a material prepared by the hydrolysis of an aluminium alkoxide or any other aluminium salt using water or a base, respectively as hydrolysing agents. The aluminium alkoxide or any other aluminium salt is called hereafter aluminium hydroxide precursor.

[0044] The hydroxides (i.e., $Ca(OH)_2$, $Mg(OH)_2$, $Ce(OH)_4$, $Ti(OH)_4$, $La(OH)_3$, ...) are preferably commercial powders of variable particle sizes (1 nm - 1 mm).

[0045] The carbonates (i.e., $CaCO_3$, $MgCO_3$, $Al_2(CO_3)_3$, $Ce_2(CO_3)_3$, $Ti(CO_3)_2$, $La_2(CO_3)_3$, ...) are preferably commercial powders of variable particle sizes (1 nm - 1 mm).

[0046] The method of preparation of supported catalysts comprises the following steps:

- Mixing the hydroxide(s) and/or carbonate(s) with the catalyst (in the appropriate proportions). The mixing is carried out in a mortar or in a ball milling apparatus for a sufficient time so that a fine powder is obtained. The catalyst and support (hydroxides and/or carbonates) are dry or contain solvents like, ethanol, methanol, water... or a mixture of solvents.
- In another process, for example the aluminium hydroxide precursor is mixed with the catalyst (in the appropriate proportions) prior to its hydrolysis. The aluminium hydroxide precursor is preferably either dry or contains a solvent.
- Drying the support-catalyst-solvent mixture by different means as air flow on a filter, rotary evaporator, vacuum pump or by the use of an oven or a furnace (heated at temperatures varying from 30 °C to 1200 °C).
- Optionally finally grinding the support-catalyst mixture in a mortar or in a ball milling apparatus for a sufficient time to obtain a fine powder of said supported catalyst.

[0047] The carbon nanotubes production on the supported catalyst by CCVD comprises the following steps:

- Spreading manually or mechanically an appropriate amount of supported catalyst on a quartz boat to be used as bed for the supported catalyst in the fixed bed reactor. In the case of a moving bed reactor, the supported catalyst is spread continuously or by intermittence mechanically or manually on the moving bed of the reactor.
- The reactor, containing the supported catalyst, is either kept initially at the appropriate constant reaction temperature (400 - 1200 °C), or it is heated to the reaction temperature for an appropriate time of the reaction. Inert or reactant gas(es) can be passed over the supported catalyst during that step.
- The pure or diluted hydrocarbon is passed over the supported catalyst at a predetermined temperature. Carbon nanotubes are grown on the supported catalyst as a result of the CCVD reaction. Diluted hydrocarbons are obtained by mixing at least one hydrocarbon with other gases such as nitrogen, argon, helium, hydrogen, CO, etc.
- The crude nanotubes, composed of a mixture of carbon nanotubes and spent supported catalyst, is collected either continuously in the case of a moving bed reactor or stepwise in the case of a fixed bed reactor.

[0048] Preferably, the carbon nanotubes purification is carried out by dissolving the spent supported catalyst as

follows:

- Stirring the crude nanotubes in a concentrated basic solution, preferably a concentrated NaOH solution, at a temperature in between 100-250°C. Recovering the solid product by filtration and preferably washing it until a neutral pH is obtained. This first step is not necessary if the catalyst support contains only Mg and/or Ca derivatives.
- Stirring the product in a concentrated acidic solution, preferably a concentrated HCl solution, at a temperature in between 0-120°C.
- Recovering the solid product (purified carbon nanotubes) by filtration and preferably washing until a neutral pH is obtained.
- Finally drying the purified carbon nanotubes by air flow on a filter or by a rotary evaporator or by the use of a vacuum pump or by the use of an oven or a furnace. Preferably, the oven or furnace is heated at temperatures varying from 30 °C to 400 °C in air or from 30 °C to 1200 °C under vacuum or inert atmosphere.

Description of a preferred embodiment of the present invention

Part I: Applying aluminium hydroxide as catalyst support *Production of aluminium hydroxide based supported catalysts*

[0049]   The production of aluminium hydroxide based supported catalysts involves the steps of obtaining the $Al(OH)_3$ support and the preparation of the supported catalyst.

i) Obtaining the Al(OH)₃ support

[0050]   The aluminium hydroxide ($Al(OH)_3$) is either a commercial powder of variable particle size (1 nm - 1 mm) or a material prepared by the hydrolysis of an aluminium alkoxide or any other aluminium salt using water or a base, respectively, as hydrolysing agent. The aluminium alkoxide or other aluminium salt is represented hereafter as aluminium hydroxide precursor.

[0051]   The aluminium hydroxide is prepared by the hydrolysis of the aluminium hydroxide precursor. Depending on the precursor, the following two examples are given:

1. The precursor is aluminium alkoxide: To 1 liter of water heated at 70-90 °C, 104.74 g of aluminium isopropoxide powder (Aldrich) was added in small quantities with vigorous stirring. After complete addition of the powder, the aluminium hydroxide gel formed is maintained at 70-90 °C while stirring for one hour. The solid is separated by filtration, dried in an air oven at 120 °C for 24 hours and ground in a mortar to get the aluminium hydroxide as a fine powder.

2. The precursor is any other aluminium salt: To 1 liter of water taken in a beaker, a salt of aluminium ($Al(NO_3)_3$, $Al_2(SO_4)_3$, $AlCl_3$, etc., for instance) is added in portions and heated to 70-90 °C to reach complete dissolution. To the hot solution of aluminium salt, 28% ammonia (or the normality equivalent of NaOH) is added drop-wise with constant stirring till the precipitation is complete. The aluminium hydroxide gel thus obtained is digested, filtered and washed with distilled water till free from the anions of the used aluminium salt. $Al(OH)_3$ gel is spread on a glass plate and dried in a hot air oven overnight at 120 °C. The solid obtained after drying is preferably ground into a fine powder in a mortar or a ball mill to get aluminium hydroxide support.

ii) preparation of the supported catalyst

[0052]   Because the catalyst particle size predetermines the diameter of the nanotubes that are obtained on said catalyst, efforts were put on the synthesis of well dispersed catalyst nanoparticles. Different "Methods" were used to prepare supported catalysts containing catalyst particles of different diameter distributions and in different chemical environments. Preferably, the supported catalysts are prepared by one of the methods, A-H described hereafter. These Methods can be classified into 4 categories:

Category 1

[0053]   The supported catalyst is produced by mixing the aluminium hydroxide powder with the catalyst (in appropriate proportions). The mixing is carried out preferably in a mortar or in a ball milling apparatus for a sufficient time so that a fine powder is obtained. The aluminium hydroxide is preferably pure. The catalyst is either dry or contains as solvent water, ethanol, methanol,... or a mixture of solvents. This category includes preferably the catalyst preparation methods A, B and C.

Method A: Production of the supported catalyst named SCA

[0054] A solution is prepared by the introduction of 2.8 g of $Co(AcO)_2.4H_2O$ and 4.7 g of $Fe(NO_3)_3.9H_2O$ in a baker, followed by the addition of 12 ml of H_2O. 40.0 g of $Al(OH)_3$ powder are introduced into a mortar. The salts solution is added to the $Al(OH)_3$ powder and mixed thoroughly for 10 minutes to obtain homogeneous powder. Finally, the solid is dried overnight in an oven at 120°C in air, cooled down to room temperature and ground into a fine powder to obtain the supported catalyst.

[0055] The supported catalyst thus prepared is optionally calcined in a furnace heated at temperatures varying from 100 °C to 1200 °C.

Method B: Production of the supported catalyst named SCB

[0056] A solution is prepared by the introduction of 2.8 g of $Co(AcO)_2.4H_2O$ and 4.7 g of $Fe(NO_3)_3.9H_2O$ in a baker, followed by the addition of 12 ml of H_2O. 40.0 g of $Al(OH)_3$ powder are introduced into a mortar. The salts solution is added to the $Al(OH)_3$ and mixed thoroughly for 10 minutes to obtain homogeneous powder. The powder is dried for 2 hours in a oven at 120°C in air, cooled to room temperature, the solid is again homogenised in a mortar and additional 6 ml of H_2O are added to the powder. The powder is mixed thoroughly for 10 minutes, and dried overnight in an oven at 120°C in air. Finally, the solid is cooled down to room temperature and ground into a fine powder to obtain the supported catalyst. Optional calcination is also applied to the supported catalyst, as in Method A.

Method C: Production of the supported catalyst named SCC

[0057] A solution is prepared by the introduction of 2.8 g of $Co(AcO)_2.4H_2O$ and 4.7 g of $Fe(NO_3)_3.9H_2O$ in a baker, followed by the addition of 48 ml of ethanol and sonication for 10 minutes. 40.0 g of $Al(OH)_3$ are added and the mixture is stirred vigorously for 10 minutes to obtain an homogeneous wet cake. The wet cake is transferred to a sintered glass filter, dried by suction for 2 hours and further dried overnight in an oven at 120°C in air. Finally, the solid is cooled down to room temperature and ground into a fine powder to obtain the supported catalyst. Optional calcination is also applied to the supported catalyst, as in Method A.

Category 2

[0058] The supported catalyst is produced by mixing the catalyst (in appropriate proportions), either with the hydro-lysing agent (water) of the aluminium hydroxide precursor (aluminium alkoxide or other aluminium salt), or with the aluminium hydroxide precursor prior to its hydrolysis. The aluminium hydroxide precursor is preferably either pure or contains a solvent. The precursor of the catalyst is preferably either pure or contains a solvent. The solvent is preferably water, ethanol, methanol,... or a mixture of solvents. This category includes preferably the catalyst preparation Method D.

Method D: Production of the supported catalyst named SCD

[0059] A solution is prepared by the introduction of 2.8 g of $Co(AcO)_2.4H_2O$ and 4.7 g of $Fe(NO_3)_3.9H_2O$ in a 2 liters round bottomed flask containing 1 liter of H_2O. The solution was heated at 70-90 °C and 104.74 g of aluminium iso-propoxide powder was added in small quantities with vigorous stirring. After complete addition of the powder, the gel formed is digested at 70-90 °C while stirring for one hour. The excess of water is then removed by a rotary evaporator and the residue is dried in an air oven at 120 °C for 24 hours and ground in a mortar to get the supported catalyst as a fine powder. Optional calcination is also applied to the supported catalyst, as in Method A.

Category 3

[0060] The supported catalyst is produced by mixing the catalyst, with aluminium hydroxide powder (in the appropriate proportions), either in a mortar or in a ball mill. This category includes preferably the catalyst preparation Methods E and F.

Method E: Production of the supported catalyst named SCE

[0061] 2.8 g of $Co(AcO)_2.4H_2O$, 4.7 g of $Fe(NO_3)_3.9H_2O$ and 40.0 g of $Al(OH)_3$ are introduced in a mortar and mixed thoroughly to obtain an homogeneous powder that is dried overnight in an oven at 120°C in air. Finally, the solid is cooled down to room temperature and ground into a fine powder to obtain the supported catalyst. Optional calcination

is also applied to the supported catalyst, as in Method A.

Method F: Production of the supported catalyst named SCF

[0062]   2.8 g of $Co(AcO)_2.4H_2O$, 4.7 g of $Fe(NO_3)_3.9H_2O$ and 40.0 g of $Al(OH)_3$ are introduced in a ball mill and milled (i.e. for 2 hours) to obtain an homogeneous powder that is dried overnight in an oven at 120°C in air. Finally, the solid is cooled down to room temperature and ground into a fine powder to obtain the supported catalyst. Optional calcination is also applied to the supported catalyst, as in Method A.

Category 4

[0063]   The supported catalyst is prepared by mixing a microemulsion containing the catalyst, with aluminium hydroxide powder (in the appropriate proportions), followed by the elimination of the solvents. This category includes preferably the catalyst preparation methods G and H.

Method G: Production of the supported catalyst named SCG

[0064]   2.8 g of $Co(AcO)_2.4H_2O$ and 2.0 g of $Fe(AcO)_2$ are dissolved in 22.8 ml of water and the solution is added to 91.2 g of CTAB (cetyltrimethylamonium bromide) dissolved in 114 g of hexanol. The solution is strongly stirred (i.e. by sonication) until it becomes clear which means that it has reached the microemulsion stable state. The microemulsion is added to 40 g of $Al(OH)_3$ and the solvents are removed by rotary evaporator. Calcination at 500 °C in air is applied to the evaporation residue for 5 hours to obtain the supported catalyst.

Method H: Production of the supported catalyst named SCH

[0065]   2.8 g of $Co(AcO)_2.4H_2O$ and 2.0 g of $Fe(AcO)_2$ are dissolved in 22.8 ml of water and the solution is added to 91.2 g of CTAB dissolved in 114 g of hexanol. The solution is strongly stirred (i.e. by sonication) until it becomes clear which means that it has reached the microemulsion stable state. The catalyst is reduced by adding dropwise, to the microemulsions kept at 5 °C under vigorous stirring, threefold excess of reducing agent (i.e. $NaBH_4$ or $NaHB(Et)_3$) dissolved in 22.8 ml of water at 0 °C. At the end of the reaction, temperature was raised to room temperature until complete hydrolysis of the excess hydride occurred. 40 g of Al(OH)3 are added to the microemulsion and the solvents are removed by rotary evaporator. Calcination at 500 °C in air is applied to the evaporation residue for 5 hours to obtain the supported catalyst.

Preferred aluminium hydroxide based supported catalysts

[0066]   The metal content of some of the preferred aluminium hydroxide based supported catalysts are represented in Table 1a. For sake of simplicity, the metal is considered as if it were introduced in the metallic form.

Table 1a:

Metal content of the preferred aluminium hydroxide based supported catalysts.								
Cat. name	Cat. prep. method	$Al(OH)_3$ (wt%)	Co (wt%)	Fe (wt%)	Ni (wt%)	Cu (wt%)	V (wt%)	Mo (wt%)
SCA1	A	96.8	3.2	-	-	-	-	-
SCA2	A	96.8	1.6	1.6	-	-	-	-
SCA3	A	96.8	-	3.2	-	-	-	-
SCA4	A	96.8	-	-	3.2	-	-	-
SCA5	A	96.8	1.6	-	1.6	-	-	-
SCA6	A	96.8	-	1.6	1.6	-	-	-
SCA7	A	96.8	-	-	1.6	1.6	-	-
SCA8	A	96.8	-	-	-	3.2	-	-
SCA9	A	96.8	1.6	-	-	1.6	-	-

Table 1a: (continued)

Metal content of the preferred aluminium hydroxide based supported catalysts.								
Cat. name	Cat. prep. method	Al(OH)$_3$ (wt%)	Co (wt%)	Fe (wt%)	Ni (wt%)	Cu (wt%)	V (wt%)	Mo (wt%)
SCA10	A	96.8	-	1.6	-	1.6	-	-
SCA11	A	96.8	-	-	-	-	3.2	-
SCA12	A	96.8	1.6	-	-	-	1.6	-
SCA13	A	96.8	-	-	-	-	-	3.2
SCA14	A	96.8	1.6	-	-	-	-	1.6
SCB2	B	96.8	1.6	1.6	-	-	-	-
SCC2	C	96.8	1.6	1.6	-	-	-	-
SCD2	D	96.8	1.6	1.6	-	-	-	-
SCE2	E	96.8	1.6	1.6	-	-	-	-
SCF2	F	96.8	1.6	1.6	-	-	-	-
SCG2	G	96.8	1.6	1.6	-	-	-	-
SCH2	H	96.8	1.6	1.6	-	-	-	-

[0067] The supported catalysts of Table 1a are tested hereafter for carbon nanotubes production by CCVD in different experimental conditions.

Evidences of the specific effect of aluminium hydroxide as catalyst support for carbon nanotubes production

[0068] To produce carbon nanotubes on the supported catalysts, the supported catalysts have to be heated at temperatures ranging from 400 to 1200 °C. The initial heating is preferably carried out in the presence of inert gases (i.e., N_2, Ar, ...) but, reactant gases (i.e., O_2, H_2, hydrocarbons, ...) can also be present. During the initial heating, water and other volatile compounds are eliminated from the supported catalyst while the active catalyst is being formed. Here active catalyst refers to metal particles, metal oxides or other metal derivatives formed during the initial heating of the supported catalyst by the reaction between the support, the catalyst and the gases. The active catalyst is responsible for the carbon nanotubes production by CCVD.

Part A: Main experiments using the supported catalyst SCA2

1. Formation of the active catalyst using N_2 as inert gas

[0069] The initial heating of the typical SCA2 supported catalyst will cause the elimination of water, acetic acid, NO_2 and O_2, thus causing a weight loss of the supported catalyst. The weight loss can be summarised as follows (starting from 47.5 g of supported catalyst SCA2) :

2.8 g of Co(OAc)$_2$.4H$_2$O	
→ 1.99 g of Co(OAc)$_2$ + 0.81 g of H$_2$O	(a: - 1.70%)
→ 0.84 g of CoO + 1.15 g of AcOAc	(b: - 2.42%)
4.7 g of Fe(NO$_3$)$_3$.9H$_2$O	
→ 2.81 g of Fe(NO$_3$)$_3$ + 1.88 g of H$_2$O	(c: - 3.96%)
→ 0.93 g of Fe$_2$O$_3$ + 1.89 g of [6 NO$_2$ + 3/2 O$_2$]	(d: - 3.97%)
40.0 g of Al(OH)$_3$	
→ 35.4 g of Al$_2$O(OH)$_4$ + 4.6 g of H$_2$O	(e: - 9.68%)
→ 30.8 g of Al$_2$O$_2$(OH)$_2$ + 4.6 g of H$_2$O	(f: - 9.68%)
→ 26.2 g of Al$_2$O$_3$ + 4.6 g of H$_2$O	(g: - 9.68%)
Maximum weight loss:	(41.09%)

[0070] The weight loss of the supported catalyst SCA2 was measured as a function of the heating time under N_2 flow at 700, 800, 900 and 1000 °C. The results are represented in Figure 1. As seen in Figure 1, the weight loss of the supported catalyst SCA2 is faster at 800 °C than at 700 °C. Nevertheless, at both of the temperatures, which are the convenient temperatures for MWNTs formation, the weight loss equilibrium is approximately reached after 10 minutes of heating under N_2 flow. Between 900 and 1000 °C that are the convenient temperatures for SWNTs formation, the weight loss is higher. However, the equilibrium of the weight loss is reached here also approximately after 10 minutes of heating under N_2 flow.

[0071] The determination of the initial time of heating under inert gases (i.e., N_2) is very important in the formation of the active catalyst. It is evident from the points which follow, that the supported catalysts prepared in the previous section have to be activated by an initial time of heating in appropriate atmosphere prior to carbon nanotubes production. The latter production is directed either to SWNTs or to MWNTs as follows:

-   The production of MWNTs was preferably carried out using 1 g of supported catalyst at 500-900°C during 1 hour using acetylene, ethylene or ethane flow of 30 ml/min and 300 ml/min of N_2 as carrier gas.

-   The production of SWNTs was preferably carried out using 4 g of supported catalyst at 900-1100 °C during 6 min. using methane flow of 250 ml/min and 1000 ml/min of H_2 or N_2 as carrier gas.

2. Formation of the active catalyst and its deactivation using C_2H_2/N_2 as reactant gas mixture

[0072] Active catalysts were formed starting from the supported catalyst SCA2 using preheating times in a flow of N_2 of 0, 10 or 60 min and, their carbon nanotubes formation activity was measured in situ. The results, in terms of carbon deposit as a function of reaction time, are represented in Figure 2. The term carbon deposit stands for: Carbon deposit (%) = 100 $(m_{crude} - m_{cat.\ dry})/m_{cat.\ dry}$ Where: m_{crude} is the mass of the as made carbon material and spent supported catalyst; $m_{cat.}$ dry is the mass of the spent supported catalyst. The carbon material is made of SWNTs, MWNTs, carbon fibers, carbon nanopaticles, amorphous carbon, pyrolytic carbon and soot in variable weight ratios. The higher the SWNTs and MWNTs content, the better the quality of the carbon material.

[0073] Figure 2 contains results from acetylene decomposition at 700 °C on SCA2, both in continuous and discontinuous processes. In this figure, the following tendencies are observed:

-   The carbon deposit is more important for a preheating time of 10 min in a flow of N_2 at 700 °C. Further preheating, up to 60 min, deactivates the catalyst progressively. Nevertheless, the lowest carbon deposit was observed in the case of no preheating in a flow of N_2 at 700 °C. It means that much less active sites are formed in this case.
-   An increase of the acetylene flow from 30 ml/min (normal flow) to 60 ml/min (high flow), keeping the nitrogen flow at 300 ml/min causes an increase of the carbon deposit (discontinuous processes in Figure 2).
-   The carbon deposit is more important for a continuous process compared to a discontinuous one.
-   The initiation step (slope at the origin of the curves in Figure 2) is very rapid and cannot be distinguished from the propagation step. In that step, the carbon "dissolved" in the active catalyst by the decomposition of the first hydrocarbon molecules diffuses out of the active catalyst and condenses to form the frontal tip of the nanotube.
-   The propagation step (first slope of the curves in Figure 2) lasts for approximately 15 or 60 min depending on, if 10 or 60 min of preheating in a flow of N_2 at 700 °C is applied, respectively. In this step, the carbon "dissolved" in the active catalyst by the decomposition of the further hydrocarbon molecules diffuses out of the active catalyst and condenses to form the body of the nanotube. It should be noted here that the carbon can also condense forming the rear tip of the nanotube, terminating the tube, and a new nanotube frontal tip.
-   The deactivation step (inflection of the curves in Figure 2) takes place at a much lower carbon deposit and reaction time when the preheating time is more than 10 min. In this step, the carbon "dissolved" in the active catalyst by the decomposition of the last hydrocarbon molecules diffuses out of the active catalyst and condenses to form either the nanotube rear tip and encapsulate the active catalyst or to encapsulate the active catalyst in the nanotube rear tip. The processes of stopping the reaction and cooling the crude product to room temperature for weighting, followed by the next reaction on the same sample (discontinuous reaction in Figure 2), enhances the deactivation of the catalyst.
-   The amorphous carbon production step (second slope of the curves in Figure 2) takes place at a much lower carbon deposit and reaction time when the preheating time is more than 10 min. In this step, the hydrocarbon molecules are decomposed on the "graphite-like" outer surface of the carbon nanotubes, to form amorphous carbon that condenses on the outer surface of the nanotubes. The second slope of the curve can be approximated to the rate of formation of amorphous carbon. The increase in the acetylene flow from 30 ml/min (normal flow) to 60 ml/min (high flow), keeping the nitrogen flow at 300 ml/min causes an increase in the amorphous carbon formation rate in the discontinuous processes of Figure 2.

Characteristics of the nanotubes:

Direct observation by TEM

[0074] The nanotubes were analysed by transmission electron microscopy with a Tecnai 10 (Philips) microscope. To prepare TEM grids, 1 mg of sample was dispersed into 20 ml of ethanol, followed by 2 minutes sonication. Then a drop was deposited on a Cu/Rh grid covered with either a vinyl polymer called formvar or holey-carbon, and the grid was dried overnight under vacuum.

[0075] The TEM observation of the samples revealed that the carbon material produced in the continuous process for 60-90 min (Figure 2) were MWNTS containing only a slight amount of amorphous carbon on the outer surface (Figures 3a and 3b). The MWNTs produced in a discontinuous process for 30 min were of same quality but represented lower carbon deposit. The MWNTs produced in continuous process for 300 min contained a little amorphous carbon, whereas the tubes from discontinuous process contained a lot of amorphous carbon. Those tubes produced in a discontinuous process under high acetylene flow (high flow curve in Figure 2) contained even more amorphous carbon.

Distribution of the carbon nanotubes

[0076] The distribution histograms of the inner and outer diameters of MWNTs, synthesised by acetylene decomposition at 700 °C in a continuous reaction of 60 min, on the supported catalyst SCA2 activated by preheating in N_2 flow for 10 min, are represented in Figure 4a. The average inner and outer diameter of the MWNTs was found to be 4.7 and 9.7 nm, respectively. No amorphous carbon is noticed either in the sample or on the walls of the tubes. The tubes are generally turbostratic with some defects in the outer surface. In the samples, MWNTs of three categories of outer diameters, i.e. thick, thin and very thin, were observed:

- MWNTs with an average inner/outer diameter of 6/25 nm and a length up to 50 μm, will be called «thick MWNTs» hereafter.
- MWNTs with an average inner/outer diameter of 4/15 nm and a length up to 50 μm, will be called «thin MWNTs» hereafter. They are generally produced in long and thick bundles.
- MWNTs with an average inner/outer diameter of 5/10 nm and a length up to 50 μm, will be called «very thin MWNTs» hereafter.

[0077] In Figure 4b, the distribution of number of walls in the as synthesized MWNTs as a function of the inner diameter is represented. These MWNTs are obtained by acetylene decomposition at 700 °C in a continuous reaction for 60 min on the supported catalyst SCA2. The supported catalyst was activated by preheating it for 10 min in a flow of N_2. The number of walls of the MWNTs is in the range of 2-26 and the average value is 8.

PIXE and PIGE analysis of the carbon nanotubes

[0078] The removal of the support and the catalyst during the purification process was followed by analysing the samples at various stages of purification by powder X ray diffraction, PIGE (Proton Induced Gamma ray Emission) and PIXE (Proton Induced X-ray Emission) techniques. PIGE analysis showed that the purified MWNTs (synthesised on SCA2 as described in the caption of Figure 3a) contained 0.1 wt% of Al. PIXE analysis of the same sample revealed the presence of 0.3 wt% of Fe and 0.2 wt% of Co.

Complementary reactions:

Effect of the weight of supported catalyst

[0079] The effect of the weight of supported catalyst on the nature of the nanotubes was studied both with (i) and without (ii) varying the velocity of the reactant gas mixture. In all the cases a spongy deposit of the carbon on the spent catalyst was obtained.

(i) When the weight of supported catalyst is varied and the velocity of the reactant gas mixture is changed proportionally in order to keep the ratio constant (constant contact time conditions), the carbon deposit was found to be constant (580%) within 2% of error (Table 1b). It means that the gases are perfectly mixed in the reactor.

Table 1b:

Effect of the change in the gas flow on the carbon deposit, keeping the contact time as a constant. Preheating time of 10 min in a flow of N_2 at 700 °C, followed by 60 min of reaction.				
SCA2 (g)	Spreading (cm)	C_2H_2 flow (ml/min)	N_2 flow (ml/min)	C deposit[a] (%)
0.062	5	7.5	75	586
0.125	10	15.0	150	570
0.187	15	22.5	225	573
0.250	20	30.0	300	589

[a]: Average carbon deposit: 580%

(ii) When the weight of supported catalyst is varied without changing the velocity of the reactant gas mixture, in a 60 min reaction, the carbon deposit decreased from 589 to 325 and then to 252% when the initial supported catalyst weight is increased from 0.25 to 0.50 and then to 1.0 g, respectively. When the weight of the supported catalyst was either 0.25 or 0.50 g, the carbon material on the catalyst was homogeneous whereas in the case when 1 g of the supported catalyst was used there was more carbon material at the entry of the gases than at the other end of the supported catalyst plate.

Effect of the acetylene flow rate

[0080] The effect of increasing the acetylene flow from 30 to 60 ml/min was similar to that observed in the discontinuous process represented in Figure 2. The same effect was also studied in a 60 min reaction of continuous process using 1.0 g of supported catalyst. It was observed that the carbon deposit increases from 252 to 349% with increasing the acetylene flow rate from 30 to 50 ml/min. Here again though the carbon material remained spongy and it was not even on the catalyst. There was more carbon material at the end where the gases enter the reactor than at the other end.

Effect of the rate of flow of acetylene gas

[0081] The effect of increasing the acetylene flow from 30 to 60 ml/min was similar to that observed in the discontinuous process represented in Figure 2. The same effect was also studied in a 60 min reaction of continuous process using 1.0 g of supported catalyst. It was observed that the carbon deposit increases from 252 to 349% with increasing the acetylene flow rate from 30 to 50 ml/min. Here again though the carbon material remained spongy and it was not even on the catalyst. There was more carbon material at the end where the gases enter the reactor than at the other end.

Effect of the rate of flow of nitrogen gas

[0082] The effect of rate of flow of nitrogen at 300, 400 and 500 ml/min was investigated, in a 60 min continuous process using 0.5 g of supported catalyst. The intention was to improve the uniformity of the carbon material on the spent catalyst. The only observation that could be made was that the higher the flow rate of N_2 gas, the lower the height of the carbon material on the spent catalyst and the deposit was more regular.

3. Formation of the active catalyst and its deactivation using C_2H_4/N_2 as reactant gas mixture

[0083] Figure 5 contains the results from ethylene decomposition on SCA2 (activated by preheating for 10 min in N_2 flow) in a discontinuous process carried out at 700, 800 and 900 °C. The results of ethylene decomposition at 700 °C in a continuous process are also represented. From this figure, the following tendencies are observed:

- At 700 °C, the carbon deposit in a 60 min continuous process is twice as high when compared with a discontinuous one. Hence, the discontinuous reaction process deactivates the catalyst.
- Comparing the curves for carbon deposit obtained in a discontinuous process at 700-900 °C, it can be concluded that the optimum reaction temperature is 700 °C. In fact, at this temperature, after the deactivation step the second slope of the carbon deposit curve is horizontal, meaning that there is no amorphous carbon deposition on the carbon nanotubes. At 800 and 900 °C, the second slopes of the carbon deposit curves, which is characteristic of the rate of amorphous carbon deposition are very small and large, respectively.

Characteristics of the nanotubes from TEM observations

[0084] Very abundant thin and very thin MWNTs, as well as some thick MWNTs, are observed on the samples produced at 700 or at 800 °C. No amorphous carbon was observed on the walls of these MWNTs, either in a continuous process (60 min at 700 °C), or in a discontinuous one (180 min at 700 or at 800 °C).
The MWNTs produced in a discontinuous process at 900 °C are covered by a very thick layer of amorphous carbon.

4. Formation of the active catalyst and its deactivation using C_2H_6/N_2 as reactant gas mixture

[0085] Figure 6 contains the results from ethane decomposition on SCA2 (activated by preheating for 10 min in N_2 flow) in a continuous process at 700, 800 and 900 °C. Results of ethane decomposition at 800 °C in a discontinuous process are also represented. On that figure, the following tendencies are observed:

- At 800 °C, the carbon deposit for a 60 min reaction is twice more important for a continuous process than for a discontinuous one. Hence, the discontinuous reaction process deactivates the catalyst.
- Comparing the carbon deposit curves of a discontinuous process at 700-900 °C, it can be concluded that the optimum reaction temperature is 800 °C. In fact, at that temperature, after the deactivation step the second slope of the carbon deposit curve is quite horizontal, meaning that there is very small amount of amorphous carbon deposition on the carbon nanotubes.

Characteristics of the nanotubes from TEM observations

[0086] Very abundant thin and very thin MWNTs, as well as some thick MWNTs, are observed on the samples produced at 700 or at 800 °C. No amorphous carbon was observed on the walls of these MWNTs, either in a continuous process (60 min at 700 or at 800 °C), or in a discontinuous one (150 min at 800 °C).
The MWNTs produced in a continuous process of 60 min at 900 °C are covered by a thin layer of amorphous carbon and islands of amorphous carbon are also observed.

5. Formation of the active catalyst and its deactivation using CH_4/N_2 as reactant gas mixture

[0087] Figure 7 contains results from methane decomposition on SCA2 (activated by preheating 10 min in N_2 flow) in a discontinuous process at 900 and at 1000 °C. On that figure, it is observed that the carbon deposit is more important at 900 °C than at 1000 °C.

Characteristics of the nanotubes from TEM observations

[0088] MWNTs and SWNTs contaminated with encapsulated metal nanoparticles, fibers and amorphous carbon were found in the samples synthesised both at 900 and at 1000 °C. The SWNTs content was more important for the samples synthesised at 1000 °C.
[0089] SWNTs synthesised by catalytic decomposition of methane were nanotubes with an average diameter of 2 nm and a length up to 10 µm. They were found both isolated and in small bundles.

6. Formation of the active catalyst and its deactivation using CH_4/H_2 as reactant gas mixture

[0090] Figure 8 contains results of methane decomposition for 6 min on SCA2 (activated by 4 min of in situ preheating from 25 to 900-1100 °C in a CH_4/H_2 flow of 75/300 ml.min^{-1}) in the presence of hydrogen at 900-1100 °C. On that figure, it is observed that the carbon deposit increases with increasing the reaction temperature up to 980 °C. Further increasing the temperature up to 1100 °C causes a decrease of the carbon deposit. The increase of the carbon deposit with increasing the temperature from 900 to 980 °C is characteristic of a better activity of the supported catalyst at higher temperatures. Oppositely, the decrease of carbon deposit with increasing reaction temperature from 980 to 1100 °C can be explained by the higher hydrogenation rate, thus eliminating the carbon deposit in a consecutive reaction, as a function of the temperature.

Characteristics of the nanotubes from TEM observations

[0091] SWNTs contaminated with MWNTs, encapsulated metal nanoparticles, fibers and amorphous carbon were found mainly on the samples synthesised at 950-1050 °C. The SWNTs content was more important for the samples synthesised at 1000 °C.

[0092] SWNTs synthesised by catalytic decomposition of methane in the presence of hydrogen were nanotubes with an average diameter of 2 nm and a length up to 10 μm. They were found both isolated and in small bundles.

Part B: Relative activity of the catalysts supported on aluminium hydroxide

[0093] The activity of all of the aluminium hydroxide based supported catalysts described in Table 1a were measured in identical reaction conditions. The comparison of their activity to produce MWNTs from acetylene decomposition is reported in Table 1c.

[0094] Acetylene decomposition on a supported catalyst for 60 min at 700 °C using 1.0 g of supported catalyst (activated by 5 min of in situ preheating from 25 to 700 °C and a 5 min plateau at 700 °C in a 300 ml.min^{-1} N$_2$ flow) and a C$_2$H$_2$/N$_2$ flow of 30/300 ml.min^{-1} is called "MWNTs-700 conditions" hereafter.

Table 1c:

Relative activity of the catalysts supported on <u>aluminium hydroxide</u> to produce nanotubes in <u>MWNTs-700 conditions</u>.					
Sup. cat. name	Metal[a]	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
				MWNTs	Am. C	Fib.
SCA1	Co	38.0	147	+++	--	---
SCA2	Co-Fe	34.5	252	+++	--	---
SCA3	Fe	34.2	72	++	+	-
SCA4	Ni	39.0	43	++	+	-
SCA5	Co-Ni	39.0	50	+++	--	---
SCA6	Fe-Ni	36.6	231	+++	--	-
SCA7	Cu-Ni	35.4	107	+	++	++
SCA8	Cu	36.5	17	+	++	+++
SCA9	Co-Cu	36.0	108	+	++	++
SCA10	Fe-Cu	34.4	53	+	++	+
SCA11	V	28.7	12	--	++	--
SCA12	Co-V	36.1	193	+++	--	+
SCA13	Mo	26.8	16	--	++	--
SCA14	Co-Mo	33.5	87	+++	--	--
SCB2	Co-Fe	34.5	257	+++	--	---
SCC2	Co-Fe	25.5	162	+++	--	---
SCD2	Co-Fe	22.1	33	++	-	--
SCE2	Co-Fe	35.0	232	+++	--	--
SCF2	Co-Fe	27.7	153	+++	-	--
SCG2	Co-Fe	7.4	93	+++	---	---
SCH2	Co-Fe	4.3	138	++	--	-

[a]: The metal, introduced as salt but considered as if it were introduced in the metallic form, does represent 3.2 wt% if single and 1.6-1.6 wt% in mixtures.

[b]: Weight loss of the supported catalyst (1.0 g) after 5 min of preheating from 25 to 700 °C and a 5 min plateau at 700 °C in a 300 ml.min^{-1} N$_2$ flow.

[c]: The quality of the carbon material was attributed as follows: +++ very high density; ++ high density; + medium density; - low density; -- very low density; --- not observed.

[0095] As seen in Table 1c, as far as individual metals are concerned, cobalt is the most active metal to produce MWNTs (147%) followed by iron (72%) and nickel (43%). Copper, molybdenum and vanadium are the least active ones (17%, 16% and 12% respectively). The activity of individual metals is in the order Co » Fe » Ni » Cu = Mo » V.

[0096] Concerning the activity to produce MWNTs of aluminium hydroxide based supported catalysts containing mixture of metals (Table 1c):

- The "method" used to prepare the supported catalyst is of importance. The Co-Fe supported catalysts were found very active if prepared by methods A, B or E, active if prepared by methods C, F or H and less active if prepared by methods G or D. Moreover, helical carbon manotubes were found on the products of methods D and F.
- Fe-Co is most active followed by Fe-Ni and Fe-Cu (252%, 231%, 53%).
- Co-Fe is most active followed by Co-V, Co-Cu, Co-Mo and Co-Ni (252%, 193%, 108%, 87%, 50%).
- Ni-Fe is most active followed by Ni-Co and Ni-Cu (231%, 107%, 50%).
- Cu-Co and Cu-Ni are equally active followed by Cu-Fe (108%, 107%, 53%).
- The activity of mixture of metals is in the order : Fe-Co > Fe-Ni > Co-V > Co-Cu = Ni-Cu > Co-Mo > Fe-Cu = Co-Ni.

[0097] Two different metal-acetates and nitrates, were used to prepare the supported catalysts and find out if the anion of the salt has any influence on the supported catalyst activity in the production of carbon nanotubes. The supported catalysts prepared from acetate salts (Table 1d) were powdery after drying at 120 °C overnight and could be easily ground further to make it a fine powder. On the other hand the supported catalysts obtained from nitrate salts were hard, stuck to the beaker after drying at 120°C, and was difficult to take out from the beaker and grind into a fine powder in a mortar or a ball mill. The results, in terms of carbon deposit, are listed in Table 1d.

Table 1d:

Relative activity of the Co-Fe/Al(OH)$_3$ supported catalyst to produce nanotubes in MWNTs-700 conditions, depending on the salts precursors.				
Sup. cat. name	Co salt	Fe salt	Weight loss[b] (%)	Carbon deposit (%)
SCA2	Co(AcO)$_2$.4H$_2$O	Fe(NO$_3$)$_3$.9H$_2$O	34.5	252
SCA2a	Co(AcO)$_2$.4H$_2$O	Fe(AcO)$_2$	34.7	192
SCA2b	Co(NO$_3$)$_2$.6H$_2$O	Fe(AcO)$_2$	30.0	188
SCA2c	Co(NO$_3$)$_3$.6H$_2$O	Fe(NO$_3$)$_3$.9H$_2$O	30.4	226

[b]: see Table 1c.

[0098] As seen in Table 1d, the effect of the anion is limited but, better results are obtained when iron nitrate is used (SCA2 and SCA2c).

Part II: Applying hydroxides, others than Al(OH)$_3$, as catalyst supports

[0099] The hydroxides, others than Al(OH)$_3$, based supported catalysts were prepared preferably using Method A. The activity of the other hydroxides based supported catalysts were measured in identical reaction conditions. The comparison of their activities to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition is reported in Tables 2a and 2b, respectively. The term "other hydroxides" stands for hydroxides of metals other than Al (i.e., Ca(OH)$_2$, Mg(OH)$_2$, Ce(OH)$_4$, Ti(OH)$_4$, La(OH)$_3$, ...).

Table 2a:

Relative activity of the catalysts supported on other hydroxides to produce nanotubes in MWNTs-700 conditions.							
Sup.	M[a]	Sup. cat. name	Weight loss[b](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
Ca(OH)$_2$	Co	SCA21	28.0	50	+++	--	--
Ca(OH)$_2$	Co-Fe	SCA22	27.9	130	+++	--	--
Mg(OH)$_2$	Co	SCA23	33.3	32	+++	--	--
Mg(OH)$_2$	Co-Fe	SCA24	35.5	99	+++	--	--
Ce(OH)$_4$	Co-Fe	SCA25	19.2	46	+++	-	+

[a-c]: see Table 1c.

Table 2a: (continued)

Sup.	M[a]	Sup. cat. name	Weight loss[b](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
Ti(OH)$_4$	Co-Fe	SCA26	14.2	12	++	++	++
La(OH)$_3$	Co-Fe	SCE27	18.0	25	+	++	--

a-c: see Table 1c.

[0100] As seen in Table 2a, the activity to produce MWNTs of mixed metals (i.e. Co-Fe) catalysts supported in other hydroxides is again higher than that of a single metal (i.e. Co). The hydroxide of Al (Table 1c) is best support followed by those of Ca, Mg, Ce, Ti and La.

[0101] Methane decomposition on a supported catalyst for 6 min at 1000 °C using 1.0 g of supported catalyst (activated by 4 min of in situ preheating from 25 to 1000 °C in the CH_4/H_2 flow) and a CH_4/H_2 flow of 75/300 ml.min^{-1} is called "SWNTs-1000 conditions" hereafter.

Table 2b:

Sup.	Metal[a]	Sup. cat. name	Weight loss[d] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
Al(OH)$_3$	Co-Fe	SCA2	39.0	16.5	-	+	+	--
Ca(OH)$_2$	Co	SCA21	30.6	10.2	--	+	++	-
Ca(OH)$_2$	Co-Fe	SCA22	29.4	5.7	--	-	++	-
Mg(OH)$_2$	Co	SCA23	34.7	3.9	--	--	+	--
Mg(OH)$_2$	Co	SCC23	29.4	2.2	++	--	+	--
Mg(OH)$_2$	Co	SCE23	33.9	8.8	--	---	+	--
Mg(OH)$_2$	Co-Fe	SCA24	37.2	12.8	+	+	+++	--
Ce(OH)$_4$	Co-Fe	SCA25	26.7	4.6	---	+	++	--
Ti(OH)$_4$	Co-Fe	SCA26	19.4	2.6	--	++	+	--
La(OH)$_3$	Co-Fe	SCE27	17.0	5.3	---	---	++	--

a, c: see Table 1c.

d: Weight loss of the supported catalyst (1.0 g) after 4 min of preheating from 25 to 1000 °C and a 6 min plateau at 1000 °C in a 300 ml.min^{-1} H$_2$ flow.

[0102] As seen in Table 2b, the activity to produce a carbon deposit on catalysts supported on hydroxides depends on the metal and on the supported catalyst preparation "Method". The hydroxide of Al is best support to produce a carbon deposit followed by those of Mg, Ca, La, Ce and Ti. Nevertheless, SWNTs were mainly observed, by TEM, on the carbon material deposited on hydroxides of Mg followed by those of Al and Ca. The supported catalyst preparation "Method" also influences its activity to produce SWNTs and, better activities are observed for supported catalysts prepared by Method C.

Part III: Applying mixed hydroxides as catalyst supports

[0103] The mixed hydroxides based supported catalysts were prepared preferably in two steps: first, thoroughly mixing the hydroxides in a mortar or a ball mill and secondly, using the mixture instead of a pure hydroxide applying Method A. The activity of mixed hydroxides based supported catalysts were measured in identical reaction conditions. The comparison of their activities to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition is reported in Tables 3a and 3b, respectively.

Table 3a:

Relative activity of the catalysts supported on <u>mixed hydroxides</u> to produce nanotubes in <u>MWNTs-700 conditions</u>.							
Sup.[e]	M[a]	Sup. cat. name	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
$Ca(OH)_2/$ $Mg(OH)_2$	Co-Fe	SCA31	34.1	122	+++	--	--
$Ca(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA32	31.1	87	+++	--	--
$Mg(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA33	34.1	65	+++	--	--
$Ca(OH)_2/$ $Mg(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA34	31.8	68	+++	--	--

[a-c]: see Table 1c.

[e]: Binary supports are in 1:1 mass ratio, ternary supports are in 1:1:1 mass ratio, and so on.

[0104] As seen in Table 3a, the activity to produce MWNTs of catalysts supported in mixed hydroxides is higher for hydroxides of Ca/Mg followed by those of Ca/Al, Ca/Mg/Al and Mg/Al.

Table 3b:

Relative activity of the catalysts supported on <u>mixed hydroxides</u> to produce nanotubes in <u>SWNTs-1000 conditions</u>.								
Sup.[e]	M[a]	Sup. cat. name	Weight loss[d](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
$Ca(OH)_2/$ $Mg(OH)_2$	Co-Fe	SCA31	34.2	8.5	+	+	++	-
$Ca(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA32	35.6	5.9	--	+	+++	-
$Mg(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA33	36.1	10.1	--	+	++	-
$Ca(OH)_2/$ $Mg(OH)_2/$ $Al(OH)_3$	Co-Fe	SCA34	36.3	7.8	---	+	+++	+

[a, c]: see Table 1c;

[d]: see Table 2b;

[e]: see Table 3a.

[0105] As seen in Table 3b, the carbon deposit is of the same order of magnitude on all of the mixed hydroxides. Nevertheless, the activity to produce SWNTs of catalysts supported on mixed hydroxides is higher for hydroxides of Ca/Mg followed by those of Mg/Al and Ca/Al.

Part IV: Applying carbonates as catalyst supports

[0106] The carbonates based supported catalysts were prepared preferably using carbonates instead of hydroxides applying Method A. The activity of the carbonate based supported catalysts were measured in different reaction conditions. The comparison of their activities to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition is reported in Tables 4a and 4b, respectively.

Table 4a:

Sup.	Metal[a]	Sup. cat. name	Weight loss[b](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
$CaCO_3$	Co	SCA41	11.2	19	+++	--	--
$CaCO_3$	Co-Fe	SCA42	7.7	83	+++	--	--
$MgCO_3$	Co	SCA43	54.6	53	++	+	-
$MgCO_3$	Co-Fe	SCA44	49.5	56	++	+	+
$Al_2(CO_3)_3$	Co-Fe	SCA45	43.2	58	--	++	--
$Ce_2(CO_3)_3$	Co-Fe	SCA46	33.8	200	+++	---	---
$La_2(CO_3)_3$	Co-Fe	SCA47	27.0	62	++	+	--

a-c: see Table 1c.

[0107] As seen in Table 4a, the activity to produce MWNTs of mixed metals (i.e. Co-Fe) catalysts supported on carbonates is again higher than that of a single metal (i.e. Co). The carbonate of Ce is best support followed by those of Ca, La, Mg and Al.

Table 4b:

Sup.	Metal[a]	41.1 Sup. cat. name	Weight loss[d] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
$CaCO_3$	Co	SCA41	42.5	11.9	-	+	++	-
$CaCO_3$	Co-Fe	SCA42	40.6	3.2	+	+	++	-
$MgCO_3$	Co	SCA43	54.3	0.6	+	--	++	--
$MgCO_3$	Co-Fe	SCA44	56.1	4.6	++	++	++	+
$Al_2(CO_3)_3$	Co-Fe	SCA45	44.8	0.4	---	---	+	--
$Ce_2(CO_3)_3$	Co-Fe	SCA46	34.4	2.0	--	++	+	-
$La_2(CO_3)_3$	Co-Fe	SCA47	37.9	12.6	---	++	++	--

a, c: see Table 1c;
d: see Table 2b.

[0108] As seen in Table 4b, the carbon deposit on catalysts supported on carbonates is more important for La and Ca carbonates, followed by Mg, Ce and Al. Nevertheless, the activity to produce SWNTS is higher on Mg carbonate, followed by that of Ca and Ce.

Part V: Applying mixed carbonates as catalyst supports

[0109] The mixed carbonates based supported catalysts were prepared preferably in two steps: first, thoroughly mixing the carbonates in a mortar or a ball mill and secondly, using the mixture instead of the hydroxide applying Method A. The activity of the mixed carbonates based supported catalysts were measured in identical reaction conditions. The comparison of their activities to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition is reported in Tables 5a and 5b, respectively.

Table 5a:

Sup.[e]	M[a]	Sup. cat. name	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
$CaCO_3/$ $MgCO_3$	Co-Fe	SCA51	28.8	16	++	+	+
$CaCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA52	26.0	9	+	+	+
$MgCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA53	29.6	24	++	+	+
$CaCO_3/$ $MgCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA54	31.8	24	+	++	+

Relative activity of the catalysts supported on mixed carbonates to produce nanotubes in MWNTs-700 conditions.

a-c: see Table 1c;
e: see Table 3a.

[0110] As seen in Table 5a, the activity to produce MWNTs of catalysts supported on mixed carbonates is low. Nevertheless, it is higher for carbonates of Mg/Al and of Ca/Mg/Al, followed by those of Ca/Mg and Ca/Al.

Table 5b:

Sup.[e]	M[a]	Sup. cat. name	Weight loss[d] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am.C	Fib.
$CaCO_3/$ $MgCO_3$	Co-Fe	SCA51	51.7	14.8	---	++	+	+
$CaCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA52	46.0	0.0	---	---	+	--
$MgCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA53	49.6	0.8	---	--	+	--
$CaCO_3/$ $MgCO_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA54	49.2	12.4	---	++	+	--

Relative activity of the catalysts supported on mixed carbonates to produce nanotubes in SWNTs-1000 conditions.

a, c: see Table 1c;
d: see Table 2b;
e: see Table 3a.

[0111] As seen in Table 5b, the carbon deposit is more important on the mixed carbonates of Ca/Mg and Ca/Mg/Al. Nevertheless, the activity to produce SWNTs of catalysts supported in mixed carbonates is very low.

Part VI: Applying mixtures of hydroxides and carbonates as catalyst supports

[0112] The mixtures of hydroxides and carbonates based supported catalysts were prepared preferably in two steps: first, thoroughly mixing the hydroxides and carbonates in a mortar or a ball mill and secondly, using the mixture instead of the hydroxide applying Method A. The activity of the mixtures of hydroxides and carbonates based supported catalysts were measured in different reaction conditions. The comparison of their activities to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition is reported in Tables 6a and 6b, respectively.

Table 6a:

Sup.[e]	M[a]	Sup. cat. name	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
Relative activity of the catalysts supported on <u>mixtures of hydroxides and carbonates</u> to produce nanotubes in MWNTs-700 conditions.							
					MWNTs	Am. C	Fib.
$Ca(OH)_2/$ $CaCO_3$	Co-Fe	SCA61	6.2	123	+	-	++
$Mg(OH)_2/$ $MgCO_3$	Co-Fe	SCA62	37.1	45	+	-	++
$Al(OH)_3/ Al_2(CO_3)_3$	Co-Fe	SCA63	28.2	40	-	--	+++
$Ca(OH)_2/$ $MgCO_3$	Co-Fe	SCA64	21.3	20	+	+	+
$Mg(OH)_2/$ $CaCO_3$	Co-Fe	SCA65	22.7	20	+	+	-

a-c: see Table 1c;

e: see Table 3a.

[0113]   As seen in Table 6a, the activity to produce MWNTs of catalysts supported on mixtures of hydroxides and carbonates is high for Ca/Ca, medium for Mg/Mg and low for Ca/Mg and Mg/Ca.

[0114]   Herringbone carbon fibers with partly hollow cores and, of regular diameter (ca. 15-70 nm) are obtained on the mixture of hydroxides and carbonates of Al. More and more irregular carbon fibers are also obtained on mixtures of hydroxides and carbonates of Ca/Ca, Mg/Mg and Ca/Mg, respectively.

Table 6b:

Support[e]	M[a]	Sup. cat. name	Weight loss[d] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
Relative activity of the catalysts supported on <u>mixtures of hydroxides and carbonates</u> to produce nanotubes in SWNTs-1000 conditions.								
					SWNTs	MWNTs	Am. C	Fib.
$Ca(OH)_2/$ $CaCO_3$	Co-Fe	SCA61	35.5	9.5	--	++	++	+
$Mg(OH)_2/$ $MgCO_3$	Co-Fe	SCA62	42.7	5.7	+	++	+	+
$Al(OH)_3/$ $Al_2(CO_3)_3$	Co-Fe	SCA63	36.0	19.0	--	++	++	-
$Ca(OH)_2/$ $MgCO_3$	Co-Fe	SCA64	38.8	10.5	-	+	++	+
$Mg(OH)_2/$ $CaCO_3$	Co-Fe	SCA65	36.0	8.8	-	++	++	+

a, c: see Table 1c;

d: see Table 2b;

e: see Table 3a.

[0115]   As seen in Table 6b, the carbon deposit is of the same order of magnitude on all of the mixtures of hydroxides and carbonates. Nevertheless, the activity to produce SWNTs of catalysts supported on mixtures of hydroxides and carbonates is higher for Mg/Mg followed by those of Ca/Mg, Mg/Ca, Al/Al and Ca/Ca.

Part VII: Applying hydroxides and/or carbonates mixed with other products as catalyst supports

[0116]   The hydroxides and/or carbonates mixed with other products based supported catalysts were prepared preferably in two steps: first, thoroughly mixing the hydroxides and/or carbonates with the other product in a mortar or a ball mill and secondly, using the mixture instead of the hydroxide applying one of the supported catalyst preparation "Methods A-H". The other products are preferably oxides (i.e. CaO, MgO, CeO_2, TiO_2, SiO_2, Al_2O_3, ...), zeolites, clays, spinels, ALPOs, etc. The activity of the hydroxides and/or carbonates mixed with other products based supported catalysts were measured in different reaction conditions and, examples are given hereafter applying CaO and/or MgO. The activities of hydroxides and/or carbonates mixed with CaO (MgO) to produce MWNTs from acetylene decomposition and, to produce SWNTs from methane decomposition are reported in Tables 7a (8a) and 7b (8b), respectively.

[0117]   The activities of catalysts supported on other products such as CaO, MgO and their mixtures were also measured under the same conditions and the results are reported in Tables 7a-b, 8a-b and 9a-b, respectively.

Table 7a:

Relative activity of the catalysts supported on CaO or on hydroxides and/or carbonates mixed with CaO to produce nanotubes in MWNTs-700 conditions.							
Support [e]	M[a]	Sup. cat. name	Weight loss[b](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
CaO	Co	SCA71	18.1	59	+++	--	--
CaO	Co	SCC71	16.5	46	+++	--	--
CaO	Co-Fe	SCA72	15.4	83	+++	--	--
CaO	Co-Fe	SCC72	16.9	173	+++	--	-
$Ca(OH)_2$/ CaO	Co-Fe	SCA73	4.5	117	+++	-	++
$CaCO_3$/ CaO	Co-Fe	SCA74	18.3	170	+++	-	+
$Mg(OH)_2$/ CaO	Co-Fe	SCA75	26.6	134	+++	-	-
$MgCO_3$/ CaO	Co-Fe	SCA76	32.4	34	+++	--	--
$Al(OH)_3$/ CaO	Co-Fe	SCA77	26.1	195	+++	--	--
$Al_2(CO_3)_3$/ CaO ·	Co-Fe	SCA78	14.6	0	+	+	+
$Ca(OH)_2$/ $CaCO_3$/ CaO		SCA79	8.0	118	+++	--	--

[a-c]: see Table 1c;
[e]: see Table 3a.

[0118]   As seen in Table 7a, the activity to produce MWNTs of the catalysts depends on the catalyst preparation method and on the metal. Co-Fe/CaO prepared by Method C is very active. The activity to produce MWNTs of catalysts supported on hydroxides and/or carbonates mixed with CaO is also very high for Al hydroxide and Ca carbonate. It is high for Mg and for Ca hydroxides as well as for the ternary mixture $Ca(OH)_2$/$CaCO_3$/CaO. Low and very low activities were observed for CaO mixed with carbonates of Mg and of Al, respectively.

Table 7b:

Support[e]	M[a]	Sup. cat. name	Weight loss[d](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
CaO	Co	SCA71	23.3	20.1	--	+	++	-
CaO	Co	SCC71	27.2	15.7	-	+	++	-
CaO	Co-Fe	SCA72	19.5	6.1	--	+	++	-
CaO	Co-Fe	SCC72	27.9	13.5	-	+	++	-
Ca(OH)$_2$/ CaO	Co-Fe	SCA73	22.0	10.7	--	++	++	+
CaCO$_3$/ CaO	Co-Fe	SCA74	30.6	13.8	---	++	+	-
Mg(OH)$_2$/ CaO	Co-Fe	SCA75	26.6	3.4	---	++	++	--
MgCO$_3$/ CaO	Co-Fe	SCA76	45.6	9.3	--	+	+	+
Al(OH)$_3$/ CaO	Co-Fe	SCA77	33.4	12.9	---	+	+	+
Al$_2$(CO$_3$)$_3$/ CaO	Co-Fe	SCA78	37.1	0.3	---	---	+	--
Ca(OH)$_2$/ CaCO$_3$/ CaO		SCA79	26.1	21.6	---	+	+++	+

Relative activity of the catalysts supported on CaO or on hydroxides and/or carbonates mixed with CaO to produce nanotubes in SWNTs-1000 conditions.

a, c: see Table 1c;
d: see Table 2b;
e: see Table 3a.

[0119]   As seen in Table 7b, the carbon deposit is higher when the catalyst support is CaO alone or mixed with hydroxides and/or carbonates of Ca. Carbon deposits of the same order of magnitude are also observed using the hydroxide of Al followed by that of Mg in mixtures with CaO. Nevertheless, SWNTs were mainly observed on CaO alone (preferably prepared by Method C) or mixed with Mg carbonate or Ca hydroxide.

Table 8a:

Support[e]	M[a]	Sup. cat. name	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
MgO	Co	SCA81	6.8	26	--	++	--
MgO	Co	SCC81	15.2	32	++	+	--
MgO	Co	SCE81	12.3	65	+	+	++
MgO	Co-Fe	SCA82	14.7	80	--	++	--

Relative activity of the catalysts supported on MgO or on hydroxides and/or carbonates mixed with MgO to produce nanotubes in MWNTs-700 conditions.

a-c: see Table 1c;
e: see Table 3a.

Table 8a: (continued)

Support[e]	M[a]	Sup. cat. name	Weight loss[b] (%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
Ca(OH)$_2$/ MgO	Co-Fe	SCA83	15.5	122	++	-	-
CaCO$_3$/ MgO	Co-Fe	SCA84	14.1	11	--	+	--
Mg(OH)$_2$/ MgO	Co-Fe	SCA85	22.6	92	++	+	-
MgCO$_3$/ MgO	Co-Fe	SCA86	35.0	61	--	++	--
Al(OH)$_3$/ MgO	Co-Fe	SCA87	21.5	90	--	++	--
Al$_2$(CO$_3$)$_3$/ MgO	Co-Fe	SCA88	11.5	23	--	++	--
Mg(OH)$_2$/ MgCO$_3$/ MgO	Co-Fe	SCA89	34.9	55	--	++	--

[a-c]: see Table 1c;

[e]: see Table 3a.

[0120]   As seen in Table 8a, the activity to produce MWNTs of catalysts supported on hydroxides and/or carbonates mixed with MgO depends on the catalyst preparation method. Moreover, high carbon deposits are not directly related to MWNTs formation. High densities of MWNTs in the carbon materials were only observed for MgO mixed with Ca or Mg hydroxides, or alone (prepared by Method C).

Table 8b:

Support[e]	M[a]	Sup. cat. name	Weight loss[d](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
MgO	Co	SCA81	11.8	4.5	---	---	++	-
MgO	Co	SCC81	11.8	3.1	+++	+	--	--
MgO	Co	SCE81	5.8	5.0	---	---	++	---
MgO	Co-Fe	SCA82	13.4	4.9	---	---	++	---
Ca(OH)$_2$/ MgO	Co-Fe	SCA83	17.0	6.7	++	-	++	-
CaCO$_3$/ MgO	Co-Fe	SCA84	27.1	12.9	+	-	++	-

[a, c]: see Table 1c;

[d]: see Table 2b;

[e]: see Table 3a.

Table 8b: (continued)

Support[e]	M[a]	Sup. cat. name	Weight loss[d](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
Mg(OH)$_2$/ MgO	Co-Fe	SCA85	25.6	8.2	--	---	++	---
MgCO$_3$/ MgO	Co-Fe	SCA86	35.5	7.9	-	-	++	---
Al(OH)$_3$/ MgO	Co-Fe	SCA87	27.1	8.1	++	-	++	++
Al$_2$ (CO$_3$)$_3$/ MgO	Co-Fe	SCA88	32.3	0.0	---	---	++	-
Mg(OH)$_2$/ MgCO$_3$/ MgO	Co-Fe	SCA89	34.4	5.3	+	+	++	+

Relative activity of the catalysts supported on MgO or on hydroxides and/or carbonates mixed with MgO to produce nanotubes in SWNTs-1000 conditions.

a, c: see Table 1c;

d: see Table 2b;

e: see Table 3a.

[0121]   As seen in Table 8b, the carbon deposit is higher when the catalyst support is MgO mixed with Ca carbonate. Carbon deposits of the same order of magnitude are also observed when the catalyst support is MgO alone or mixed with other supports but Al carbonate. Nevertheless, SWNTs were mainly observed on MgO alone (prepared by Method C) or mixed with hydroxides of Al or Ca. Mixtures of MgO with Ca carbonate, together or not with Mg hydroxide, are also good catalysts supports to produce SWNTs. Lower and lower activities to produce SWNTs were observed for binary mixtures of MgO with Mg carbonate and Mg hydroxide, respectively.

Table 9a:

Support[e]	M[a]	Sup. cat. name	Weight loss[b](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]		
					MWNTs	Am. C	Fib.
CaO/MgO	Co	SCC91	11.7	27	++	+	--
CaO/MgO	Co-Fe	SCC92	8.4	44	+++	+	-

Relative activity of the catalysts supported on CaO/MgO to produce nanotubes in MWNTs-700 conditions.

a-c: see Table 1c;

e: see Table 3a.

[0122]   As seen in Table 9a, the mixture CaO/MgO is a good catalyst support to produce MWNTs. Nevertheless, better activity was observed applying Co-Fe than Co.

Table 9b:

Support[e]	M[a]	Sup. cat. name	Weight loss[d](%)	Carbon deposit (%)	Quality of the carbon material from TEM[c]			
					SWNTs	MWNTs	Am. C	Fib.
CaO/MgO	Co	SCC91	17.6	10.5	++	--	++	--
CaO/MgO	Co-Fe	SCC92	20.8	0.2	+	+	++	--

Relative activity of the catalysts supported on <u>CaO/MgO</u> to produce nanotubes in <u>SWNTs-1000 conditions</u>.

[a, c]: see Table 1c;
[d]: see Table 2b;
[e]: see Table 3a.

[0123] As seen in Table 9b, the mixture CaO/MgO is a good catalyst support to produce SWNTs. Nevertheless, better activity was observed applying Co than Co-Fe.

Part VIII: Evidences of metal migration from catalyst supports to carbon nanotubes during nanotubes synthesis

[0124] Crude MWNTs samples were first analysed by PIGE and PIXE to establish their metal content and, the results are represented in Table 10a. Secondly, the spent supported catalysts were completely removed from the crude nanotubes samples by repeated dissolutions in concentrated HCl and/or in concentrated NaOH depending on the catalyst support to produce purified nanotubes. The complete removal of the spent supported catalysts was monitored by powder X ray diffraction. Afterwards, the purified nanotubes were analysed by PIXE and PIGE to measure the content of metals incorporated in the nanotubes and, the results are presented in Table 10b.

Table 10a:

Support	Supported catalyst and related metal (M) from the support						PIGE (wt%)	PIXE (wt%)		
	Al	Ca	Mg	Ce	Ti	La	M	M	Co	Fe
Al(OH)$_3$	SCA1	-	-	-	-	-	18.6	-	1.6	-
Al(OH)$_3$	SCA2	-	-	-	-	-	8.6	-	0.3	0.3
Ca(OH)$_2$	-	SCA21	-	-	-	-	-	26.4	1.8	-
Ca(OH)$_2$	-	SCA22	-	-	-	-	-	20.3	0.3	0.4
Ca(CO$_3$)	-	SCA41	-	-	-	-	-	22.9	1.9	-
Ca(CO$_3$)	-	SCA42	-	-	-	-	-	12.4	0.2	0.3
CaO	-	SCA71	-	-	-	-	-	27.6	0.8	-
CaO	-	SCA72	-	-	-	-	-	21.3	0.3	0.4
Mg(OH)$_2$	-	-	SCA23	-	-	-	22.7	-	2.0	-
Mg(OH)2	-	-	SCA24	-	-	-	13.3	-	0.8	1.0
Mg(CO$_3$)	-	-	SCA43	-	-	-	24.8	-	2.8	-
Mg(CO$_3$)	-	-	SCA44	-	-	-	27.8	-	1.2	1.2
MgO	-	-	SCC81	-	-	-	34.2	-	1.1	-
Ce(OH)$_4$	-	-	-	SCA25	-	-	-	58.8	0.5	0.6
Ce$_2$(CO$_3$)$_3$	-	-	-	SCA46	-	-	-	38.1	0.4	0.5
Ti(OH)$_4$	-	-	-	-	SCA26	-	-	34.5	0.9	1.1

Metal content of crude MWNTs samples before removal of the spent supported catalysts.

Table 10a: (continued)

Metal content of crude MWNTs samples before removal of the spent supported catalysts.										
Support	Supported catalyst and related metal (M) from the support						PIGE (wt%)	PIXE (wt%)		
	Al	Ca	Mg	Ce	Ti	La	M	M	Co	Fe
La(OH)$_3$	-	-	-		-	SCA27	-	55.2	0.5	0.2
La$_2$(CO$_3$)$_3$	-	-	-	-	-	SCA47	-	43.2	0.5	0.4

Table 10b:

Metal content of purified MWNTs samples after complete removal of the spent supported catalysts.										
Supported catalyst and related metal (M) from the support						Puri. step	PIGE (wt%)	PIXE (wt%)		
Al	Ca	Mg	Ce	Ti	La		M	M	Co	Fe
SCA1	-	-	-	-	-	f	-	-	3.2	-
SCA2	-	-	-	-	-	f	0.1	-	0.2	0.3
						g	0.1	-	0.01	0.02
						h	0.1	-	0.01	0.02
-	SCA21	-	-	-	-	i	-	0.2	7.2	-
-	SCA22	-	-	-	-	i	-	0.1	0.9	0.9
-	SCA41	-	-	-	-	i	-	0	6.1	-
-	SCA42	-	-	-	-	i	-	0	0.8	1.2
-	SCA71	-	-	-	-	i	-	0.3	4.6	-
-	SCA72	-	-	-	-	i	-	0	0.2	0.5
-	-	SCA23	-	-	-	i	0.1	-	0.6	-
-	-	SCA24	-	-	-	i	0.4	-	0.5	1.3
-	-	SCA43	-	-	-	i	0.4	-	3.3	-
-	-	SCA44	-	-	-	i	0.01	-	0.9	2.7
-	-	SCC81	-	-	-	i	0.01	-	1.4	-
-	-	-	SCA25	-	-	f	-	-	0.4	1.7
-	-	-	SCA46	-	-	f	-	-	0.3	0.5
-	-	-	-	SCA26	-	f	-	-	0.8	1.3
-	-	-		-	SCA27	f	-	-	1.0	1.3
-	-	-	-	-	SCA47	f	-	-	0.6	1.0

f: Repeated consecutive dissolution of the spent supported catalyst in NaOH solution and in HCl solution.

g: Applying step f twice.

h: Applying step g followed by breacking of the nanotubes during 3 days in a ball mill, and applying step f again.

i: Dissolution of the spent supported catalyst in HCl solution.

[0125] As seen in Table 10b, metals from the catalyst supports (i.e. Al, Mg, Ca, Ce, La, Ti) are incorporated in the carbon nanotubes during their synthesis. As these metals are not removable by acidic dissolution and as they are also present in carbon nanotubes that do not contain encapsulated metal nanoparticles, it was deduced that they are in interstitial positions, at nanotubes defects.

General conclusions:

[0126]

- The catalyst support plays a very important role because it is part of the catalyst chemical environment, thus determining its activity. It also influences the catalyst particle size.
- The convenient catalyst particle size (ca. 5-20 nm in diameter) for thick MWNTs synthesis involves preferably the use of a single metal (preferably Co) and water as solvent in the catalyst preparation method.
- To obtain thin MWNTs, mixture of metals are more convenient and water (in microemulsion or alone) is still a favourite solvent. In fact, in mixture of metals, each individual metal is further dispersed by the other, hence decreasing the catalyst particle size down to ca. 2-12 nm in diameter.
- To obtain very thin MWNTs, mixture of metals are again more convenient but alcools (i.e. ethanol, methanol) are best solvents to produce catalyst particles of ca. 1-8 nm in diameter.
- Catalyst nanoparticles (preferably Co) of ca. 1-5 nm in diameter, dispersed in a catalyst support using preferably an alcool (i.e. ethanol, methanol), is best catalyst to produce SWNTs. The use of mixture of metals increases the production of other carbon structures during SWNTs synthesis.

Claims

1. Single and/or multiple-wall carbon nanotubes which may contain interstitial metals obtainable by a preparation process comprising at least a catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said support comprising hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

2. Single and/or multiple-wall carbon nanotubes as in claim 1, **characterised in that** the interstitial metals are selected from the group consisting of Al, Mg, Ca, Ce, La, and Ti.

3. Carbon fibres obtainable by a preparation process comprising at least a catalytic step using at least a catalytic system, said catalytic system comprising a catalyst and a support, said support comprising hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

4. Carbon nanotubes and/or carbon fibres as in any of the previous claims **characterised in that** the support of the catalytic system comprises carbonates selected from the group of $CaCO_3$, $MgCO_3$, $Al_2(CO_3)_3$, $Ce_2(CO_3)_3$, $Ti(CO_3)_2$, $La_2(CO_3)$ and/or mixtures thereof.

5. Carbon nanotubes and/or carbon fibres as in any of the previous claims, **characterised in that** the support of the catalytic system comprises hydroxides selected from the group of $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Ce(OH)_4$, $Ti(OH)_4$ $La(OH)_3$ and/or mixtures thereof.

6. Carbon nanotubes and/or carbon fibres as in any of the previous claims, **characterised in that** the support of the catalytic system comprises oxides selected from the group consisting of Al_2O_3, CaO, MgO, CeO_2, TiO_2, SiO_2 and/ or mixtures thereof.

7. Catalytic system for the preparation of single and/or multiple-wall carbon nanotubes and/or for the preparation of carbon fibres, said catalytic system comprising a dispersion of nanoparticles containing metals at any oxidation state in hydroxides and/or carbonates or mixtures thereof and said metals being selected from the group consisting of Fe, Co, Ni, V, Cu, Mo, Sn and/or mixtures thereof.

8. Single and/or multiple-wall carbon nanotubes **characterised in that** said nanotubes comprise interstitial metals.

9. Process for the preparation of single and/or multiple-wall carbon nanotubes, comprising at least a catalytic step using a catalytic system, said catalytic system comprising a catalyst and a support, said catalyst being selected from the group consisting of metals and/or metal oxides and/or metal derivatives **characterised in that** said support is selected from the group consisting of hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

10. Process for the preparation of carbon fibers by a catalytic system in a catalytic step, said catalytic system com-

prising a catalyst and a support, said catalyst being selected from the group consisting of metals and/or metal oxides and/or metal derivatives **characterised in that** said supports are selected from the group consisting of hydroxides and/or carbonates or mixtures thereof with or without metal oxides.

11. Process as in claim 9 and 10, **characterised in that** the support of the catalytic system comprises carbonates selected from the group of $CaCO_3$, $MgCO_3$, $Al_2(CO_3)_3$, $Ce_2(CO_3)_3$, $Ti(CO_3)_2$, $La_2(CO_3)_3$ and/or mixtures thereof.

12. Process as in claim 9 and 10, **characterised in that** the support of the catalytic system comprises hydroxides selected from the group of $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Ce(OH)_4$, $Ti(OH)_4$, $La(OH)_3$ and/or mixtures thereof.

13. Process as in claim 9 and 10, **characterised in that** the support of the catalytic system comprises oxides selected from the group consisting of Al_2O_3, CaO, MgO, CeO_2, TiO_2, SiO_2 and/or mixtures thereof.

14. Process as in claim 9 to 13, **characterised in that** the catalytic step is performed between 500 and 900°C in order to prepare multi-wall nanotubes and between 900 and 1100°C in order to prepare single-wall nanotubes.

15. Use of a catalytic system as in claim 7 for the preparation of single and multi-wall nanotubes.

16. Use of a catalytic system as in claim 7 for the preparation of carbon fibers.

17. Use of the nanotubes as in claim 1,2,4,5 or 6 for the storage of hydrogen.

18. Use of nanotubes as in claim 1,2,4,5 or 6 for applications in semi-conductors and transistors.

19. Use of a catalytic system as in claim 7 or obtainable by a process according to claim 9 to 14 for the preparation of hydrogen.

FIG. 1: SCA2/Nitrogen
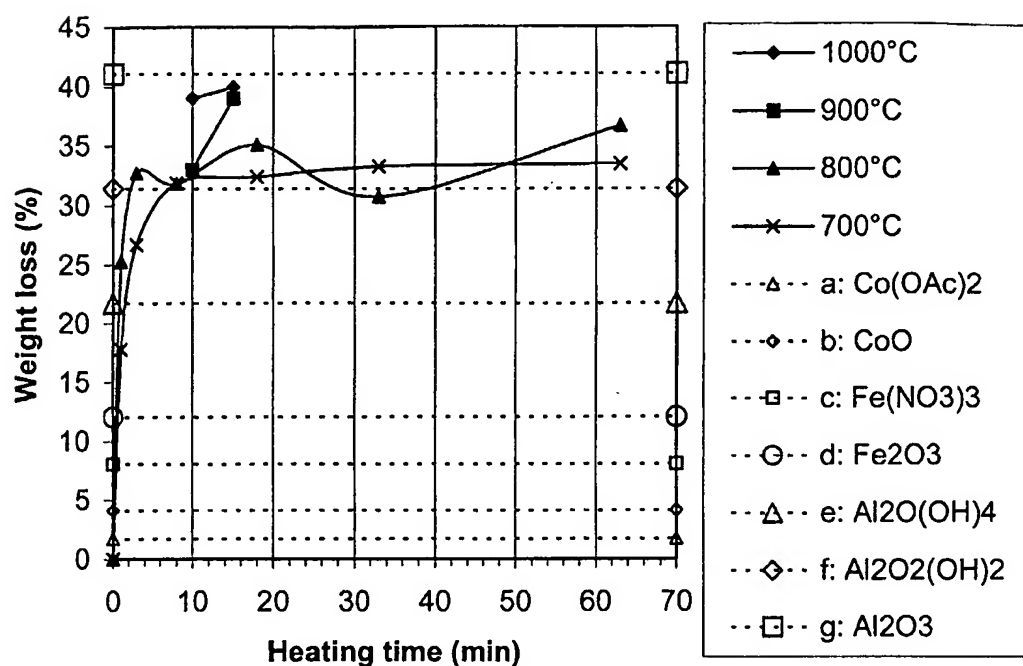
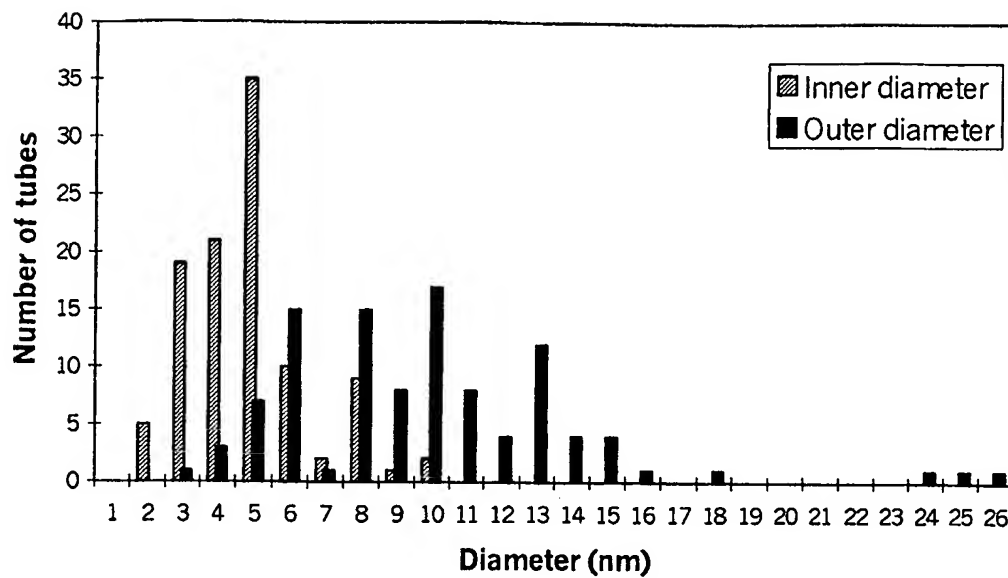FIG. 2: SCA2/Acetylene/Nitrogen
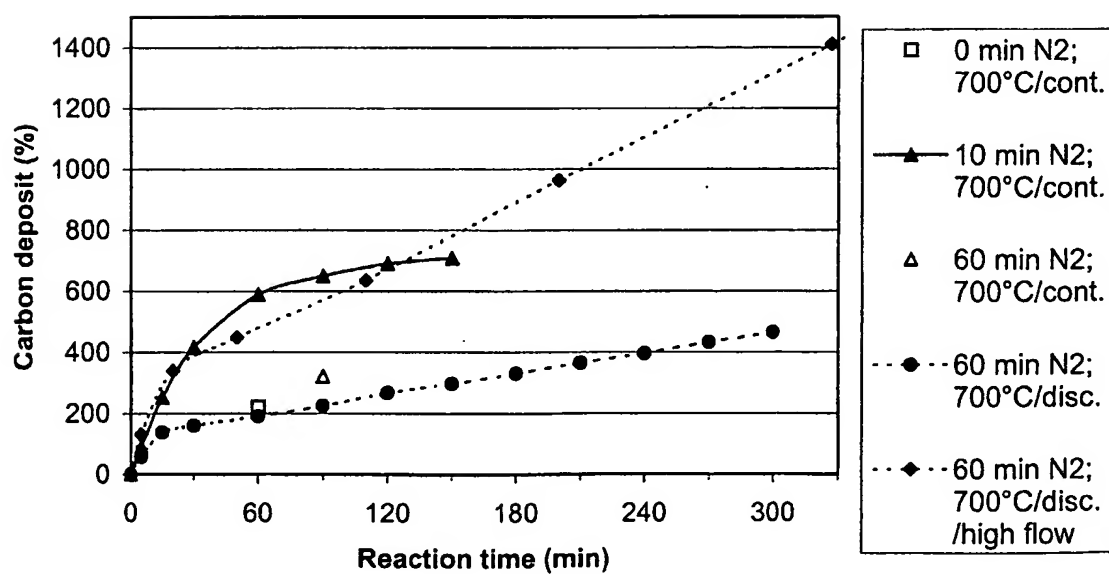
Fig.3a
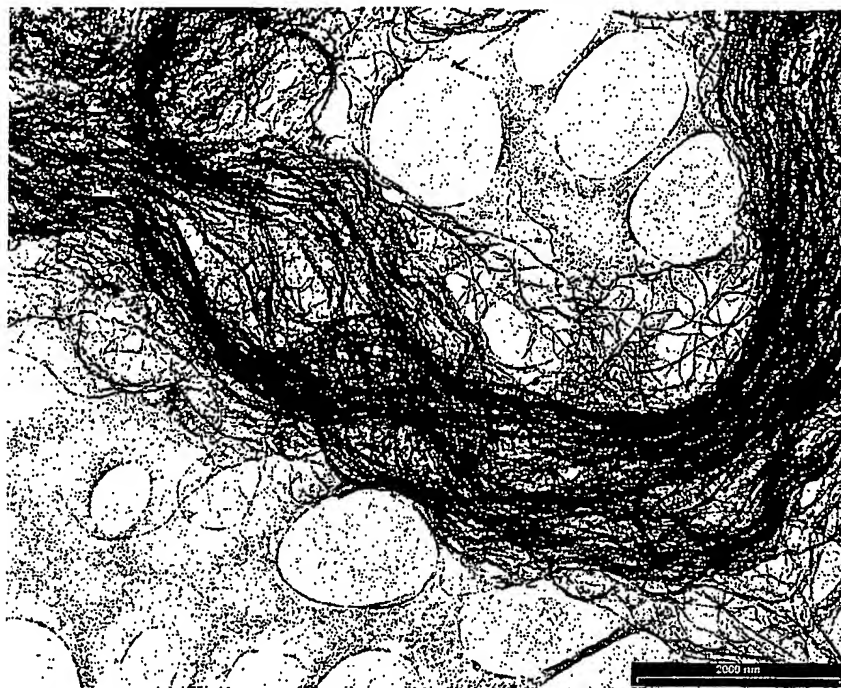
Fig.3b

Fig. 3c

Fig. 3d
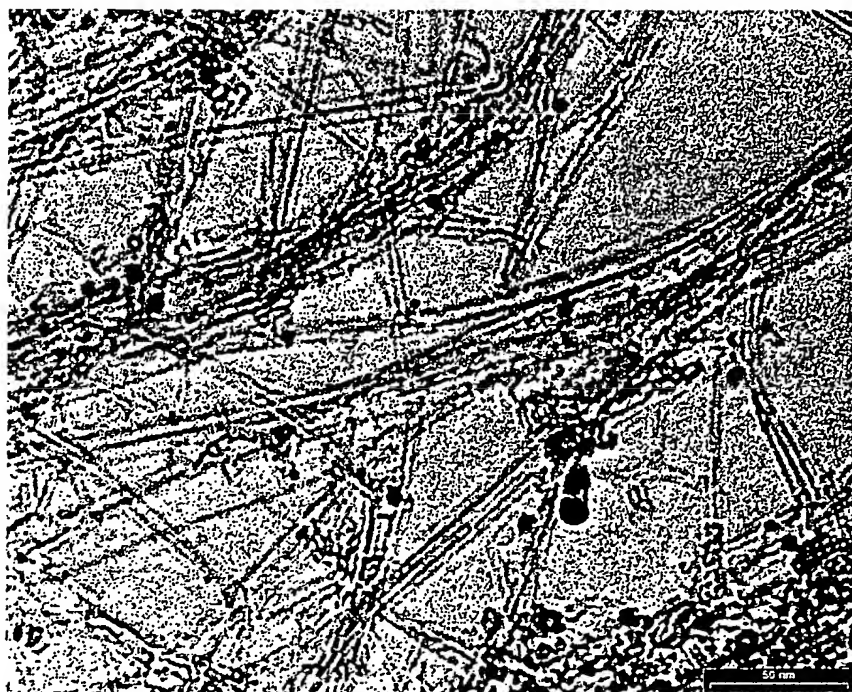
Fig. 4a

Fig. 4b
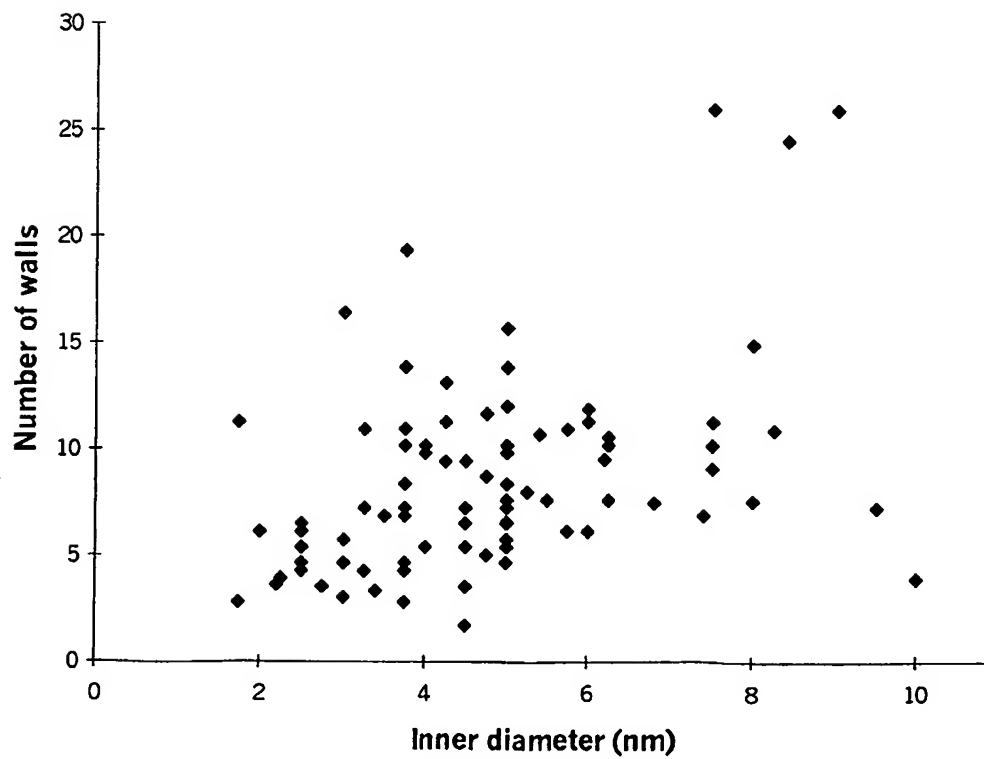
Fig. 5 : SCA2/Ethylene/Nitrogen

Legend:
- 10 min N2; 700°C/cont.
- 10 min N2; 900°C/disc.
- 10 min N2; 800°C/disc.
- 10 min N2; 700°C/disc.

X-axis: Reaction time (min)
Y-axis: Carbon deposit (%)
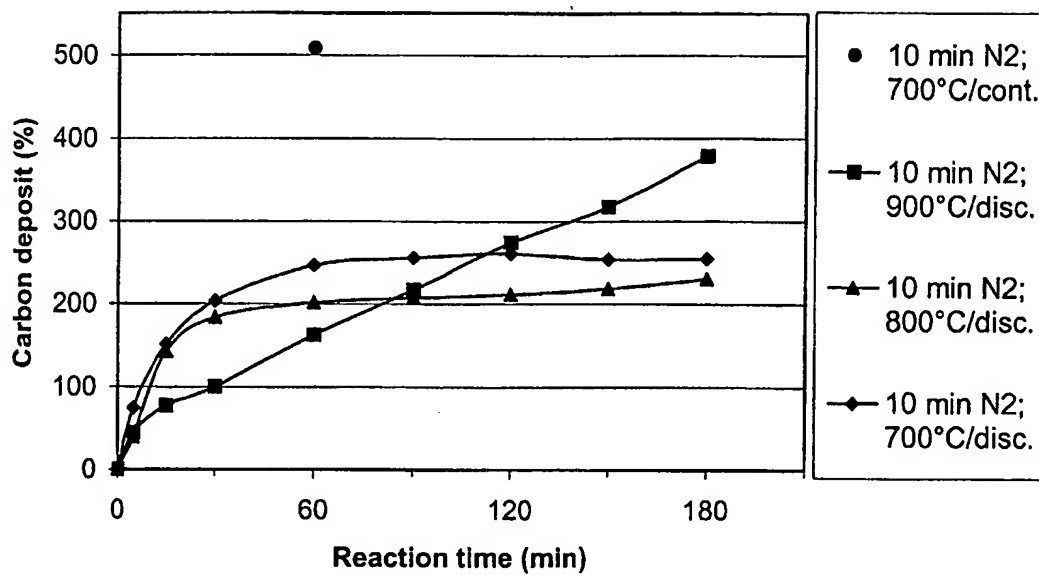
Fig. 6 : SCA2/Ethane/Nitrogen

Legend:
- 10 min N2; 900°C/cont.
- 10 min N2; 800°C/cont.
- 10 min N2; 700°C/cont.
- 10 min N2; 800°C/disc.

X-axis: Reaction time (min)
Y-axis: Carbon deposit (%)
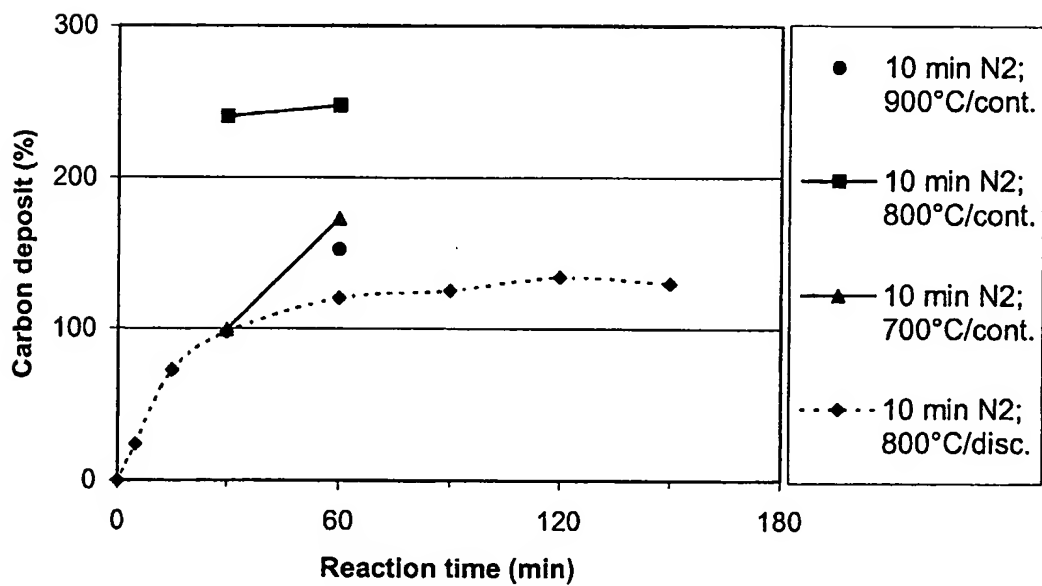
Fig.7 : SCA2/Methane/Nitrogen
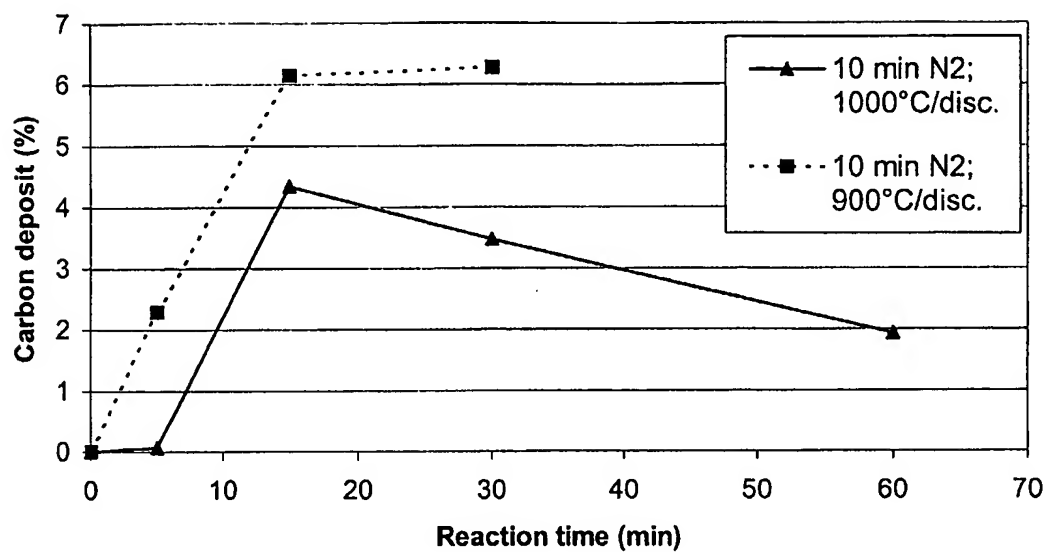
Fig. 8 : SCA2/Methane/Hydrogen

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EUROPEAN SEARCH REPORT

Application Number

EP 01 87 0268

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Place of search	Date of completion of the search	Examiner
THE HAGUE	26 April 2002	Rigondaud, B

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L : document cited for other reasons

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L : document cited for other reasons
& : member of the same patent family, corresponding
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